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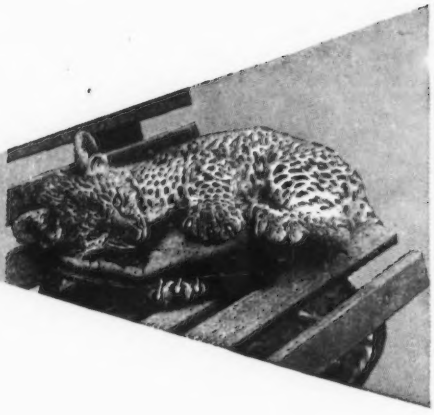

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The Journal

of the

AMERICAN LEATHER CHEMISTS ASSOCIATION

Vol. LV JANUARY 1960 No. 1

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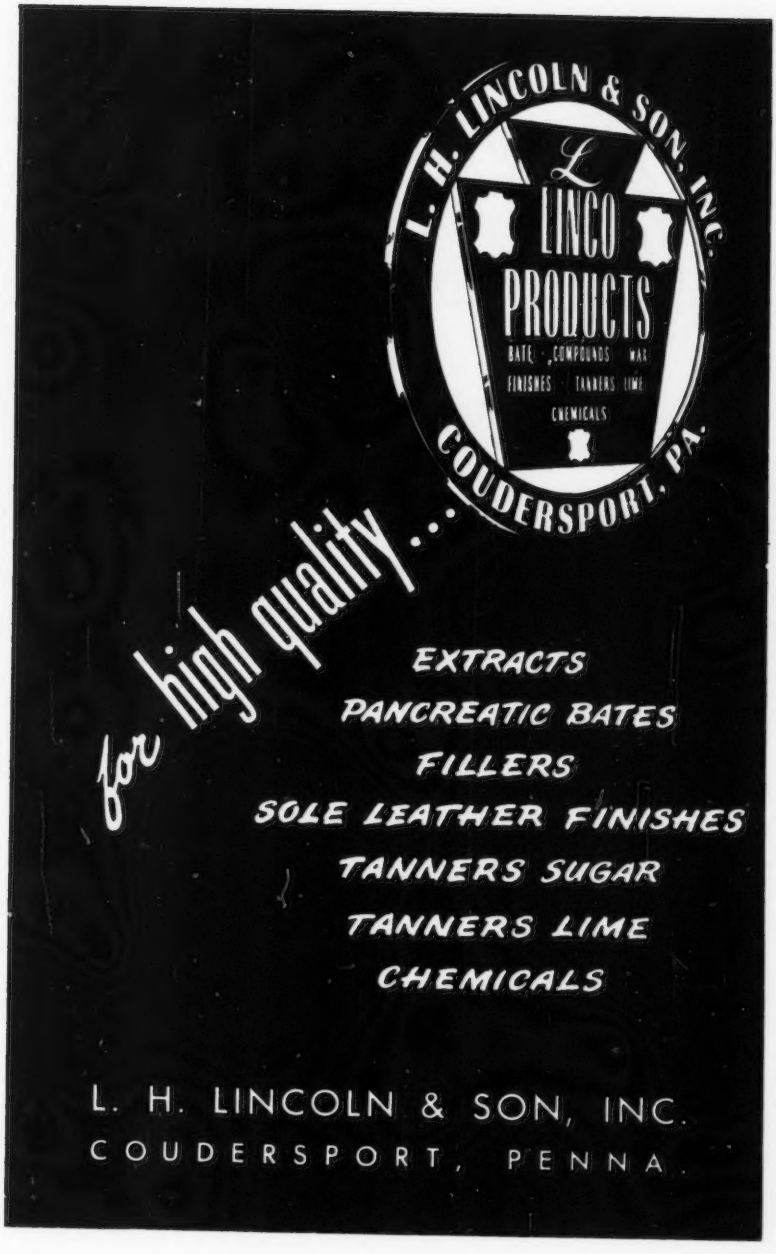
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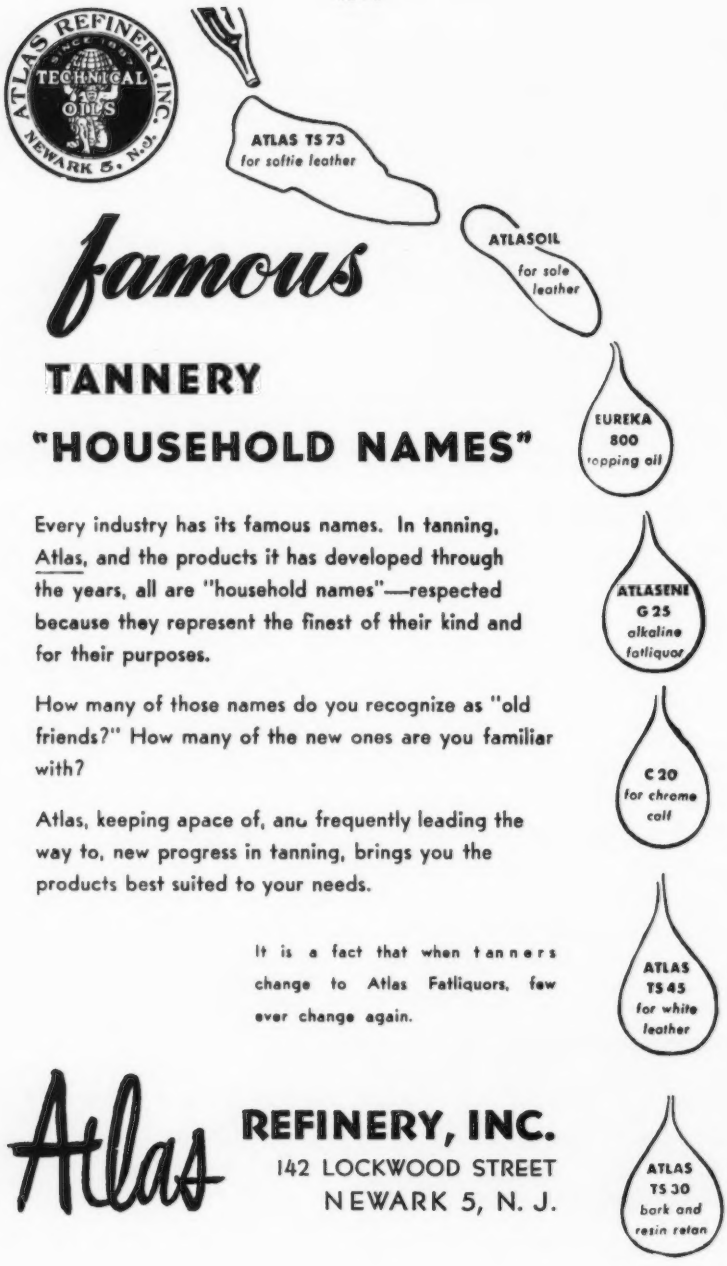

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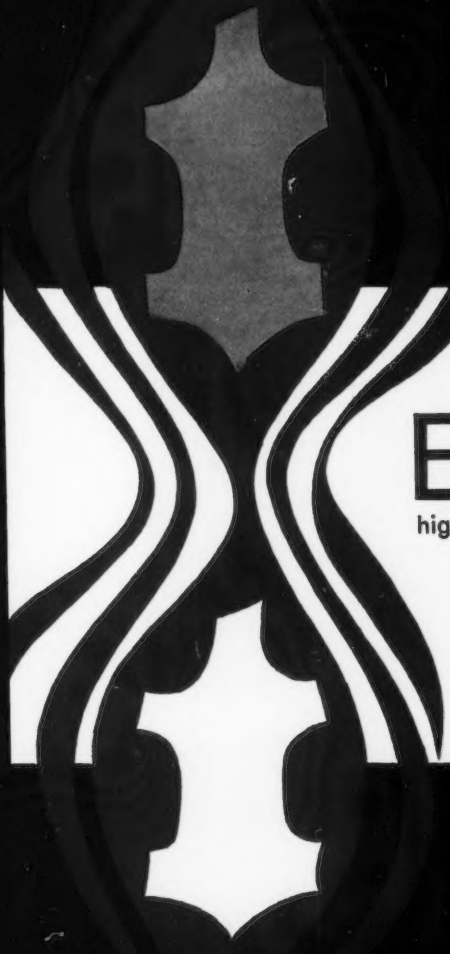

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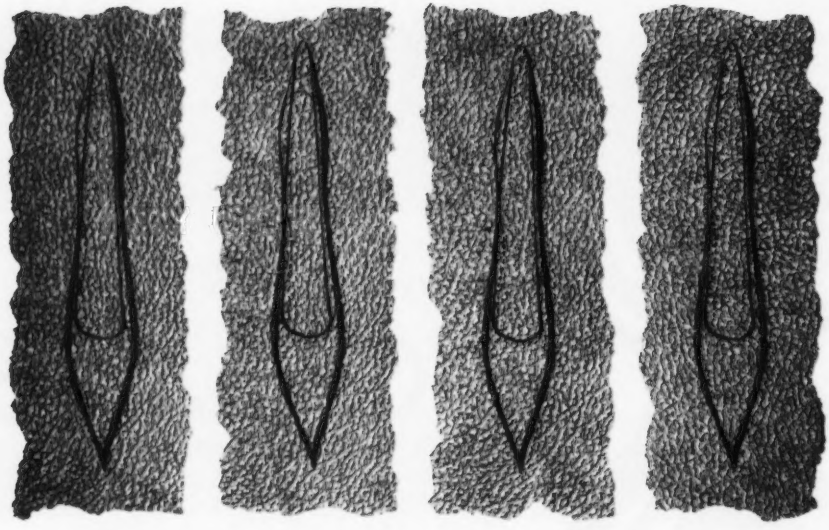

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NOTES FOR CONTRIBUTORS

The following notes are intended to be of assistance to authors submitting papers for publication in this *Journal*. They will be repeated in the January issue each year and should be kept for reference.

General.—It is the objective of the *Journal* to publish papers in all fields pertaining to leather. The papers will normally fall into three broad categories: (1) those which describe basic or fundamental research and make a new contribution to knowledge; (2) those which describe applied research on methods or processes and represent technical progress in leather production, evaluation, or use; and (3) those which review some theoretical or practical aspect of leather chemistry.

Submission of a paper will be held to mean that it will not be published elsewhere unless rejected. It is understood that papers delivered at the annual meeting will be submitted to this *Journal* for consideration and within a reasonable length of time. Papers accepted for publication should not be republished elsewhere in the same form without permission of the Editor.

Form of paper.—It is requested that two copies of a manuscript be submitted to the Editor. Since each manuscript will be sent to at least two reviewers, two copies will expedite editorial action.

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Authors should refer to current issues of the *Journal* to familiarize themselves with the typographical conventions, layout of tables, citation of references, etc. Manuscripts which deviate significantly from the form of the *Journal* will be returned for rewriting.

Papers should be headed by a brief and informative title followed by the names of the authors and the location in which the work was conducted. If the name of the senior author is not placed first, his identity should be indicated in a footnote. The names of authors should be followed by an abstract telling why the work was done and summarizing the results and their significance briefly. The over-all arrangement of the text is somewhat flexible, although it is desirable to subdivide a paper into sections. These should include an adequate summary of previous literature in the field, including relevant patents. References are to be numbered consecutively in parentheses, not alphabetically. The experimental section must describe the work accurately and in sufficient detail so that it may be repeated by others.

Credits should be given in an Acknowledgment section at the end of the text. The names of journals should be abbreviated in accordance with the practice of *Chemical Abstracts* and this *Journal*. The one exception is the name of this *Journal* which is abbreviated as *JALCA*. Literature citations must be complete, including authors' initials, volume and page numbers, and year. "In press" references are discouraged.

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Life Lines.—A brief biography of each author of a manuscript is to be supplied with the manuscript. If a previously printed biography is up-to-date and satisfactory, this should be indicated, together with a reference to the issue of the *Journal* in which it appeared.

THE MECHANICAL PROPERTIES OF COLLAGEN AND LEATHER FIBRES*

F. R. MORGAN

British Leather Manufacturers' Research Association

ABSTRACT

This paper reviews the recent British Leather Manufacturers' Research Association work in the field of fibre physics. The chief object of this work has been to compare the strength and breaking extension of raw and tanned fibres. It has included a study of the effect of different test conditions on the strength and breaking extension of raw fibres, and an investigation of the influence of different kinds of straight vegetable and chrome tannage upon fibre strength and extensibility.

Work with collagen fibres is not easy because, in the first place, it is not possible to obtain fibres longer than a few centimetres; and secondly, fibres taken from the same small piece of pelt and apparently similar in all respects very often exhibit wide differences in physical properties. The difficulty of restricted fibre length can be overcome by the use of specially designed apparatus and refinements in experimental technique, while fibre variability requires careful experiment design and the examination of a large number of samples to give truly representative results. Most previous experiments on collagen fibres have been at a particular disadvantage in this respect, and attempts have been made to draw firm conclusions from insufficient data.

Experiments with raw fibres have shown that changes in test conditions lead to large and well established changes in fibre strength and extensibility. The results suggest that fibre plasticity increases with increase in relative humidity, and that the mechanism of fibre breakdown depends on the rate of loading. In particular, there is an optimum rate of loading which depends on the humidity and which gives maximum strength and breaking extension: it is about 12 g/min for humidities of less than about 70%. Changes in humidity also produce changes in strength, and raw fibres are strongest in the intermediate range of humidities.

*This paper was delivered at the Annual Meeting of the Society of Leather Trades Chemists at Leeds, England, in September, 1959. It is a summary of work which will be covered in greater detail in a series of three papers to be published in the Journal of the Society of Leather Trades Chemists. The first paper will appear in the January, 1960, issue.

The results for tanned fibres show that variations in vegetable or chrome tannage (within the limits set by normal tannery practice) produce only small changes in fibre strength and breaking extension, and fibres heavily tanned are little, if any, different from those lightly tanned. The overall effect of tannage manifests itself as a loss in fibre strength and breaking extension. Weight for weight, tanned fibres are weaker and less extensible than raw ones.

The research described in this paper provides valuable background information which not only serves as a basis for applied research on practical problems (such as the wear resistance of sole leathers and the lasting properties of upper leathers) but also enables a fuller understanding of some of the processes associated with leather manufacture to be obtained.

INTRODUCTION

In recent years increasing attention has been devoted to problems concerned with the mechanical and physical properties of both natural and synthetic fibres. Some time ago a programme of research on the mechanical properties of collagen and leather fibres was started in the B.L.M.R.A. laboratories. Work on fibres is never easy, and collagen fibres are probably more difficult to work with than others for two reasons. In the first place, it is not possible to obtain collagen fibres longer than a few centimetres, and any investigation of mechanical properties therefore requires the measurement of length to a high order of accuracy. Secondly, fibres taken from the same piece of pelt and apparently similar in all respects very often exhibit wide differences in mechanical properties. The difficulty of restricted fibre length can be overcome by the use of specially designed apparatus and refinements in experimental technique, while fibre variability requires careful experimental design in accordance with statistical principles so that a reliable estimate of experimental error can be obtained, together with the examination of a large number of specimens in order to obtain truly representative results.

The work that will be described in this paper has no direct practical application in leather manufacture. However, a knowledge of the mechanical and physical properties of collagen fibres, and the way they are altered by tannage, is of very considerable importance, since the physical properties of any leather cannot be fully evaluated until the properties of its constituent fibres have been determined. This kind of work is important for two other reasons. In the first place it should lead to a better understanding of the tanning process and of the structure of fibres, and secondly it will provide the type of information which is required as a basis for applied research on practical problems such as the wear resistance of sole leathers and the lasting properties of upper leathers.

The need to study fibre properties has been recognised by leather scientists for some time. Credit for being the first to work in this field must go to the Swiss workers Jovanovits and Alge, who studied vegetable-tanned fibres and published their results in 1932. Soon after this an extensive study of fibre properties was undertaken by the Russians Pchelin and Ginsberg; but their results are not generally known in this country because their papers were published in a Russian scientific journal and never translated. In the past ten years or so work has also been reported from America, where Highberger and Compton have independently studied the influence of tannage upon strength, and Mao and Roddy have examined the effects of tannery processes upon the same property. To complete this review mention must be made of papers which have originated in this country: Conabere and Hall have investigated the tensile strengths of fibres taken from commercially tanned leathers, and Mitton has reported an extensive series of experiments on fibres taken from vegetable-tanned commercial steer hide belly. Hall has also described a series of experiments on wet raw collagen fibres, and Mitton and Morgan have investigated the speed at which vegetable tannage occurs by studying changes in fibre extensibility during tannage.

This paper deals in the main with recent B.L.M.R.A. work in the field of fibre physics. The chief object of this work has been to compare the strength and breaking extension of raw and tanned fibres, but various other points have been investigated as well. Thus the programme has included a study of the effect of different test conditions on the strength and breaking extension of raw fibres that had been previously subjected to different loading histories, and an investigation of the influence of different kinds of straight vegetable and chrome tannage upon fibre strength and extensibility. In addition, the form of the collagen stress-strain curve has been determined under different conditions. This, of course, represents an extensive programme of work and has, in fact, so far involved the examination of over 2000 fibres.

EXPERIMENTAL

The fibres used in this work were taken from a wet-salted cow hide. To facilitate removal of the fibres small pieces of the hide were soaked in water and then partly dried: the fibres were then teased out, using a small pair of tweezers and a couple of stout needles. Only fibres, or, more strictly, fibre bundles, longer than about 1¼ cm. and free from branching and other obvious faults were retained, and when a fairly thick fibre was obtained no attempt was made to split it into thinner fibres if it appeared reasonably compact, although such subdivision would have been possible in most cases. The fibres were thoroughly washed in several changes of distilled water, dehydrated in five changes of acetone, and then dried at 40°C. for 24 h.

As mentioned above, this work has been chiefly concerned with measurements of fibre strength and breaking extension. These measurements are made in an extensiometer developed specially for this work (Fig. 1). This

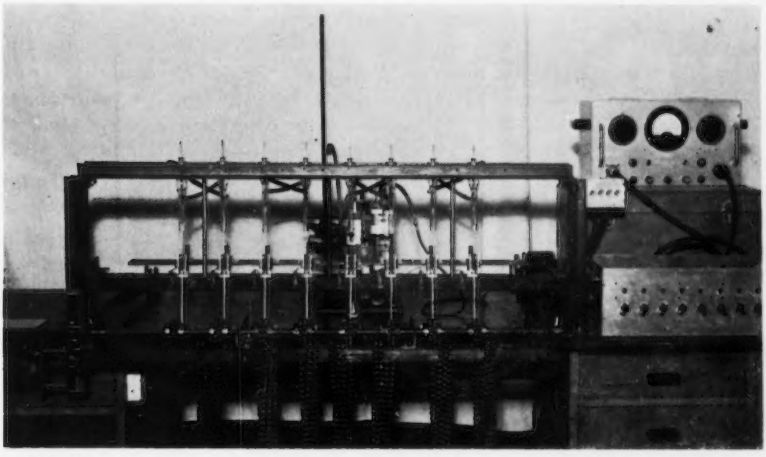

FIGURE 1.—General view of the extensiometer. The loading chains are driven through the gear-box on the left, and the electronic apparatus for the measurement of fibre extensions can be seen on the right. [Figures 1, 2, and 3 are reproduced through the kind permission of the Editor of the *Journal of Scientific Instruments*, England.]

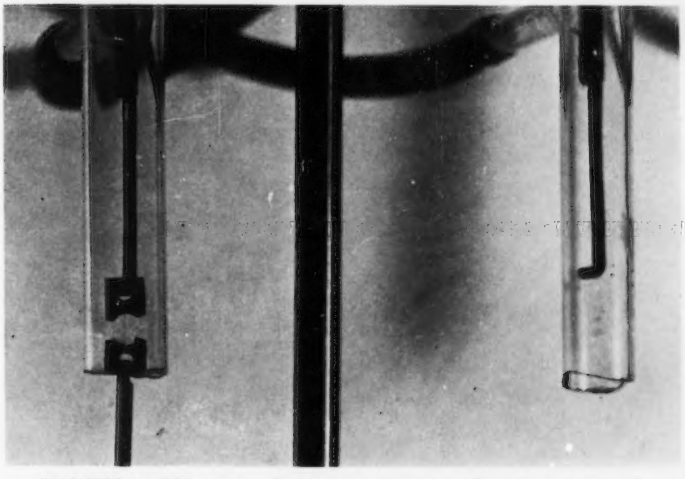

FIGURE 2.—Fibre set up in the extensiometer and ready to be tested.

provides for tests to be made on eight fibres simultaneously with control of the relative humidity of the ambient air and also rate of loading. Loads of up to about 450 g. are applied chainometrically and extensions of the order of 10^{-5} cm. are measured by an electronic method which depends on the change in electrical capacity produced by a change in separation between two metal plates. Fibres were mounted for test in this extensiometer in two ways: either they were tied and glued to small copper hooks or they were glued across a hole in a piece of stout card which was cut through immediately before the fibre was tested so as to leave it free to extend. Figure 2 shows a card-mounted fibre in the extensiometer and ready for test.

Since collagen fibres are extremely irregular in cross-section, no attempts were made to measure actual fibre thicknesses. It was therefore not possible to obtain results for tensile strength, and instead another measure of fibre strength (much used in the textile industry) known as the breaking length, was used. The breaking length is obtained by dividing the breaking load by the fibre weight per unit length. It is equivalent to the specific strength, or the tensile strength divided by the density, and since it has the dimension of length, the usual unit is the kilometre. Another property of the breaking length is that it is the length of uniform fibre that would just break under its

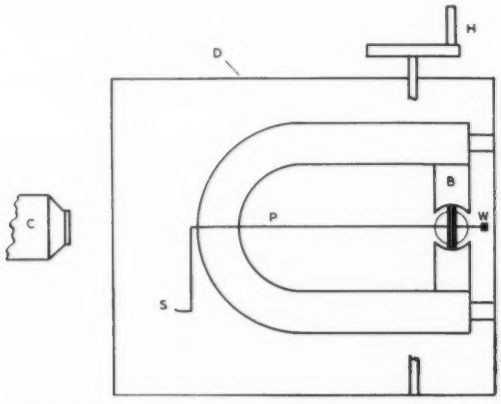

FIGURE 3.—General view of the electromicrobalance. A weight placed in the scale pan deflects the pointer of the moving-coil milliammeter movement, and a current is then passed through the movement to return it to the equilibrium position. The associated electrical control circuit is not shown in this diagram.
B—Meter movement
C—Microscope
D—Dust-proof perspex box
H—Zero adjustment handle
P—Pointer
S—Scale pan
W—Counterbalance weights

own weight when freely suspended from one end. A determination of fibre weight per unit length is necessary to calculate the breaking length, and in this work an electromicrobalance sensitive to about one microgram was used for this (Fig. 3). This balance consists of a sensitive moving-coil milliammeter movement used as a torsion balance, and permits accurate and rapid weighing to be done.

Work On Raw Fibres

In this experiment the effect of humidity and rate of loading upon the strength and breaking extension of raw fibres was investigated. In addition to this, some of the fibres used in this work were mechanically conditioned in different ways, by extending them with a known load a given number of times, before they were broken in the extensiometer. This mechanical conditioning was done to determine whether repeated loading of a fibre leads to a progressive loss of strength or breaking extension—in other words, a fatigue effect. The experimental conditions are summarised in Table I.

TABLE I

MECHANICAL PROPERTIES OF RAW FIBRES

Mechanical Conditioning: Fibres stretched 1½%, 3%, 4½%, or 6% of initial length 0, 1, 5, or 25 times. This done at 0% R.H. or 100% R.H., and stretching load applied twice a second or once every 5 seconds.

Test Conditions: Breaking load applied at rate of 3 g/min, 6 g/min, 12 g/min, or 24 g/min with humidity of 0% R.H., 33% R.H., 66% R.H., or 100% R.H.

Results

General remarks.—This work on raw fibres involved tests on 512 samples. They were mounted between small copper wire hooks and varied in initial length from 2 mm. to 12 mm., and they varied in weight from about 10 micrograms per cm. to about 250 micrograms per cm. The mean initial length and weight per unit length was 6.85 mm. and 127.2 micrograms per cm. respectively, and these fibres were found to have an average breaking load of 141.0 g., an average breaking length of 19.7 km., and an average breaking extension of 24.9%. The results obtained in this experiment illustrate well the variability found when measurements of this kind are made on fibres. Thus Fig. 4 shows the distribution of values of breaking load. In this figure the height of the column at any interval of the load axis indicates the number of fibres which had breaking loads in that interval. Although most fibres had breaking loads of between 30 g. and 160 g., it will be seen that the full range of breaking loads extends from about 10 g. to over 600 g. This result (which, as will be seen later, is not merely due to differences in fibre weight

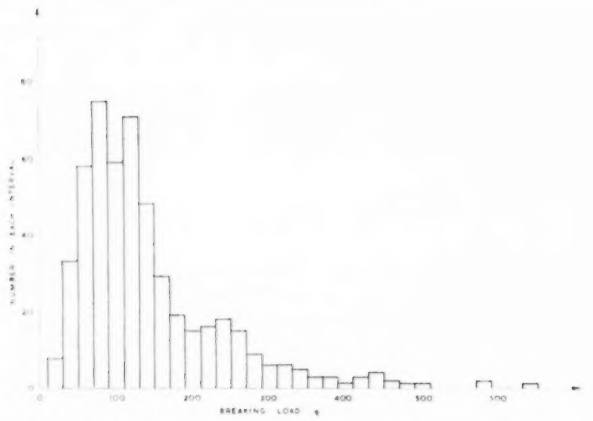

FIGURE 4.—Raw fibres. Diagram showing the distribution of breaking loads.

or thickness), of course, emphasises the importance of careful experimental planning in accordance with statistical principles and the necessity of tests on many specimens. Only by proceeding in this way is it possible to obtain a reliable estimate of error and thus to calculate the precise significance of the results. It is in just this respect that most previous experiments on collagen fibres have been at a disadvantage. Here it was found that, even with this large number of fibres, average breaking loads and breaking extensions differing by 13 g. and 1.6% respectively were necessary to establish the real effect of any factor varied in this experiment.

Effect of mechanical conditioning.—The fibres that were mechanically conditioned in different ways gave results for strength and extension that were closely similar, and any changes due to this mechanical conditioning were small. The results are summarised in Table II, which shows that, on the

TABLE II

RAW FIBRES: EFFECT OF MECHANICAL CONDITIONING

No. of Times Fibres Stretched	0	1	5	25	Means
Breaking Load, g.	149.0	132.0	144.0	138.0	141.0
Breaking Extn. %	26.0	23.6	24.5	23.9	24.9

average, mechanical conditioning leads to a small drop in strength and breaking extension. The changes in breaking load shown in this table are not significant, however, and it must be concluded that changes of this magni-

tude are probably caused by random variations in fibre strength rather than by changes in the experimental conditions. On the other hand, changes in breaking extension of the magnitude shown here are significant: mechanical conditioning reduces the breaking extension because a fibre, once stretched, does not return to its initial length when released but suffers a permanent residual extension. The average residual extension was found to be about one third of the extension under load in this experiment.

Effect of test conditions

(*a*) Humidity.—Changes in test conditions resulted in fairly large and therefore well-established changes in fibre strength and extensibility. The effect of humidity is shown in Fig. 5. Changes due to humidity were similar at all rates of loading, and this figure therefore gives average results for strength (the full line) and extensibility (the broken line). At low humidities an increase in humidity gives increases in both strength and extensibility. However, as the humidity is raised above about 35% changes in breaking extension become small while the breaking load falls steadily as saturation is approached, and moist fibres are weaker than dry ones. These changes are probably due to changes in fibre plasticity. At low humidities little plastic flow is possible, the fibre is therefore relatively brittle, and strength and extensibility are low. As the humidity is raised plastic flow occurs more readily and fibril components which are stressed can slip relative to others. The resultant redistribution of stress permits higher breaking loads and breaking extensions to be reached. However, near saturation slip occurs so readily that it causes premature breakdown and the strength decreases.

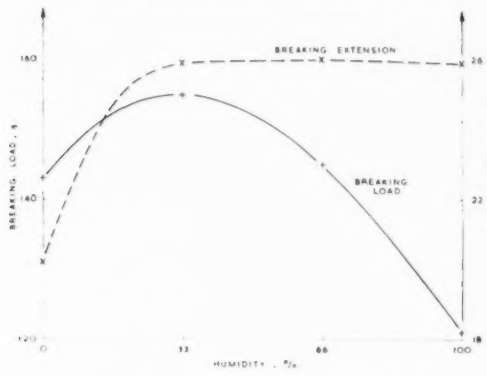

FIGURE 5.—Raw fibres. Effect of humidity on strength and breaking extension.

(*b*) Rate of loading.—Large differences in breaking load and breaking extension occurred when the rate of loading was changed. Figure 6 shows that the average breaking extension was a maximum at a rate of loading of 12 g/min. It fell rapidly at lower rates than this, and more slowly as the rate was increased. The changes in breaking load at different rates of loading

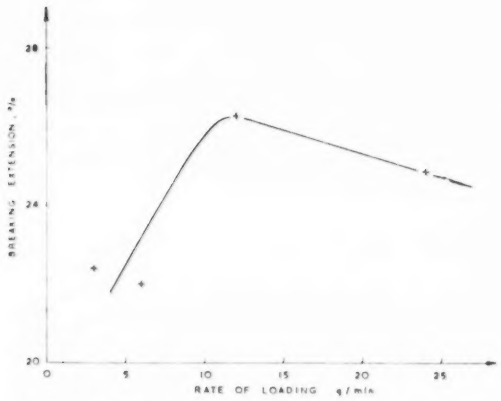

FIGURE 6.—Raw fibres. Effect of rate of loading on breaking extension.

are shown in Fig. 7. These changes were influenced by humidity only when it approached saturation. For this reason the average results for fibres tested at 0%, 33%, and 66% R.H. are shown on one curve in this figure, and a second curve shows the results for fibres tested at 100% R.H. The shape of these curves (and the results for breaking extension shown in Fig. 6) may be explained by assuming that the mechanism of fibre breakage undergoes a change as the loading rate is increased. In general, when a fibre is stretched to the breaking point, some fibril components are probably stretched taut before others. If the fibre is moist, plastic flow occurs readily, and stressed fibrils slip relative to others to redistribute the total load. At saturation, therefore, continued application of a constant load may eventually cause breakdown by slip, while the same load for a shorter time does not cause rupture: thus, breaking load increases with rate of loading. At lower humidities, slipping of fibrils occurs less readily, and some fibrils become stressed and broken before others are stretched taut, although some redistribution of stress is possible if the stretching is slow. There is therefore an optimum rate of loading such that sufficient slip occurs for redistribution of stress but little breakdown by fibril

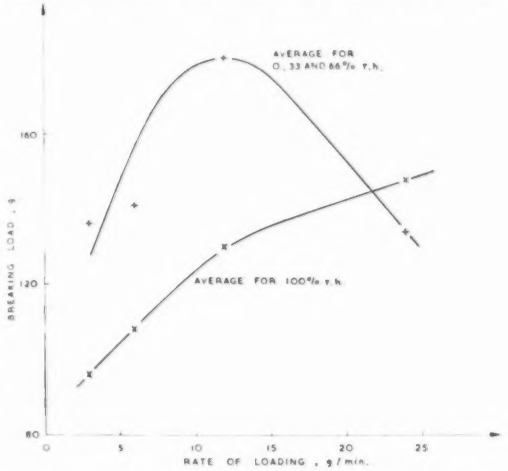

FIGURE 7.—Raw fibres. Effect of rate of loading on strength.

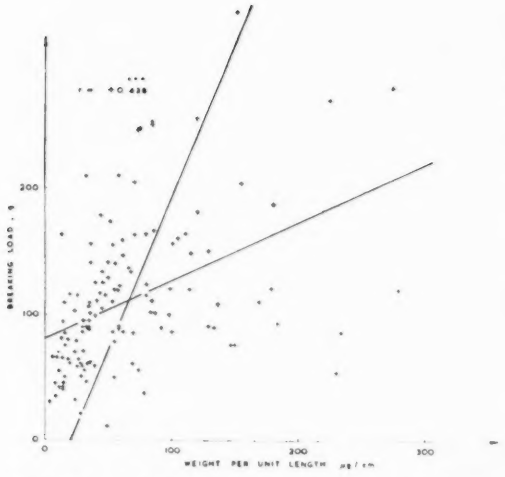

FIGURE 8.—Raw fibres. Scatter diagram showing effect of weight per unit length on breaking load. Note that even fibres with approximately the same values of weight per unit length exhibit wide differences in breaking load.

slip. The results obtained here (Fig. 7) suggest that the critical rate of loading is about 12 g/min. for humidities below saturation. At 100% R.H. the curve shows no maximum, and the optimum rate of loading is presumably above 24 g/min. This dependence of the optimum rate on the humidity is expected, since the plasticity of collagen fibres increases at high humidity, and this permits the plastic flow mechanism to operate at higher loading rates.

Effect of variation in fibres: influence of fibre weight and initial fibre length upon strength and extensibility.—The fibres tested in this experiment were randomly selected from a stock of several thousand: they therefore varied in weight per unit length and, after they had been mounted, had initial lengths of from about 2 mm. to about 12 mm. Fibre strength, and possibly also breaking extension, must depend upon weight per unit length. Also, initial fibre length probably influences strength and breaking extension, since fibres vary along their length; and long fibres should therefore be weaker and less extensible than short ones, since the strength of a fibre is no greater than that of its weakest part. The easiest way to study the effect of weight per unit length upon breaking load is simply to plot the results on a graph. This has been done in Fig. 8. This figure shows that even fibres with closely similar values of weight per unit length

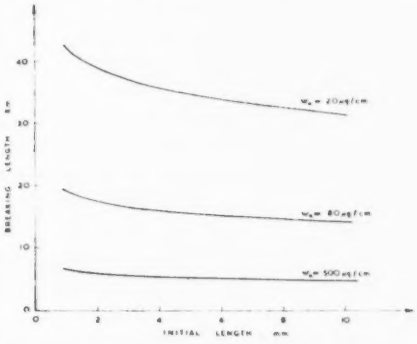

FIGURE 9.—Raw fibres. Effect of initial length on strength.

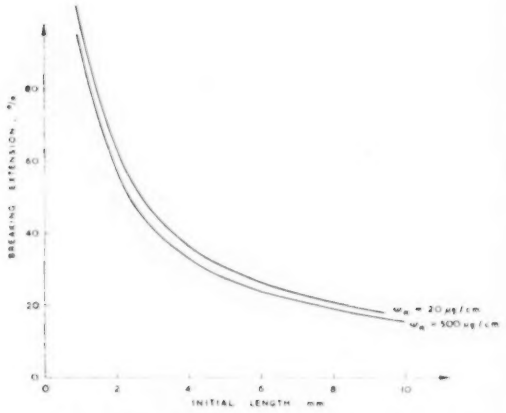

FIGURE 10.—Raw fibres. Effect of initial length on breaking extension.

exhibit wide variations in breaking load, and more important, it suggests that strength is not proportional to weight per unit length (strict proportionality requires that the regression line of breaking load on weight per unit length to pass through the origin) but proportional to some power of the weight per unit length. This graphical method of analysis is quick and easy, but it is of only limited usefulness in this case because strength and breaking extension depend upon both fibre weight per unit length and initial length. It is therefore necessary to use multiple

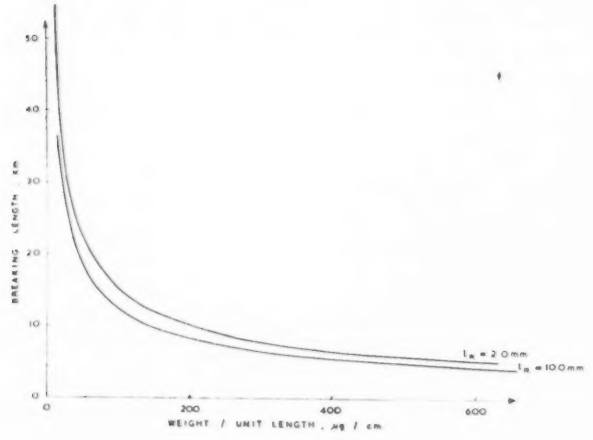

FIGURE 11.—Raw fibres. Effect of weight per unit length on breaking length. The breaking length decreases as the weight per unit length increases: thus thin fibres are relatively stronger than thick.

regression techniques to calculate the effect of simultaneous variations in initial length and weight per unit length. This calculation shows that changes in fibre weight per unit length and initial length account between them for about 60% of the variation in strength and 45% of the variation in breaking extension. It also confirms that long fibres are weaker and less extensible than short ones, and that thin fibres are relatively stronger than thick. These results are shown graphically in Figs. 9, 10, 11, and 12.

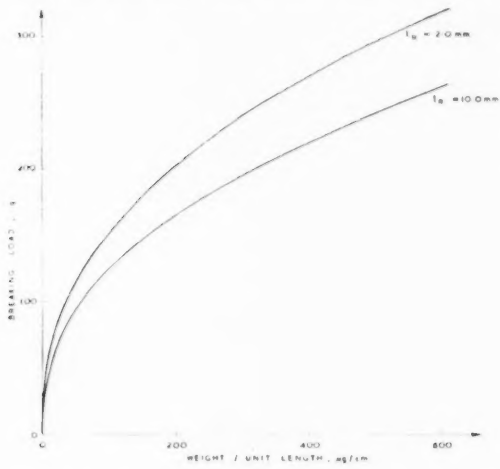

FIGURE 12.—Raw fibres. Effect of weight per unit length on breaking load. Note that an increase in weight per unit length does not give a proportional increase in breaking load.

Work On Tanned Fibres

The work on tanned fibres was undertaken to investigate the effect of different methods of tannage on fibre strength and breaking extension. Both vegetable and chrome tannages have been studied in separate experiments involving respectively 1024 and 512 fibres. The fibres used in these tannage experiments were sewn into small pieces of muslin, and each was put, together with a small piece of acetone-dehydrated pelt, into a test tube. The piece of pelt enabled a normal liquor-to-goods ratio to be maintained. Pretanning and tanning treatments were carried out in the test tubes, and each fibre could in this way be individually tanned in accordance with the experiment plan. The experimental conditions are outlined in Table III, which deals with the vegetable tannages, and Table IV, which deals with the chrome. It must be emphasized that although a great number of different methods of tannage were tried in these experiments, care was taken not to go outside the limits set by normal tannery practice: a large number of modifications in processing were involved, but nevertheless no revolutionary tannages were attempted.

TABLE III

VEGETABLE TANNAGE OF FIBRES

Lime: $Ca(OH)_2$, pH 12.5, 30 minutes or 8 days

Delime: 5% NH_4Cl, final pH 8

Type of Tan: Mimosa, sulphited quebracho, myrobalans, or chestnut.

1st. and 2nd pits	*Strength:*	15° Bk. to 100° Bk.
	pH:	3.0 to 4.5
	Time:	2 to 14 days
Hot-pit	*Strength:*	140° Bk.
	Temp.:	35° C. or 40° C.
	Time:	0 to 7 days
	pH:	2.8 or 3.2

Washed, dried, mounted between cards

Test Conditions	Loading Rate:	6 g/min
	Humidity:	0, 33, 66, or 100% R.H.

TABLE IV

CHROME TANNAGE OF FIBRES

Lime: $Ca(OH)_2$, pH 12.5, 30 minutes or 3 hours

Delime: 5% NH_2Cl, final pH 8

Bate: 1% Pancreol 3A, 30 minutes at 40° C.

Pickle: Four different liquors; salt and acid amounts varied

Chrome Tan	*Time:*	30 minutes to 14 days
	Cr_2O_3 offered:	¼% to 6¾% on wet-pelt weight
	Basicity:	0% to 40%.

Basification: to pH 3.5 or 4.2, 0.1% $NaHCO_3$ solution, time same as time in tan.

"Horse", Neutralise: 1% $NaHCO_3$ solution.

Fat-liquor: 3% sulphated fish oil, 30 minutes at 40° C., agitated.

Washed, dried at room temperature, mounted between cards

Test Conditions	*Loading Rate:*	6 g/min
	Humidity:	0, 33, 66, or 100 R.H.

Results

Effect of variations in tannage.—In general, changes in strength as a result of modifications in tannage were found to be small. Now, this result raises several important points, and it therefore warrants further consideration. In these experiments the conditions were varied so that some fibres would receive a light, and others a heavy, tannage. Nevertheless, the fibre strength might have been almost independent of the method of processing because all

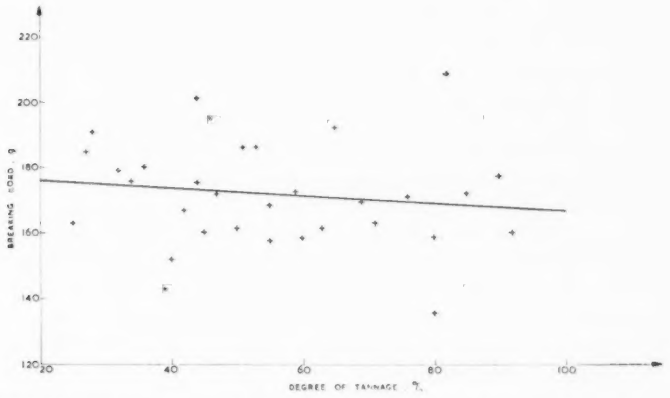

FIGURE 13.—Vegetable-tanned fibres. Scatter diagram showing effect of degree of tannage on strength.

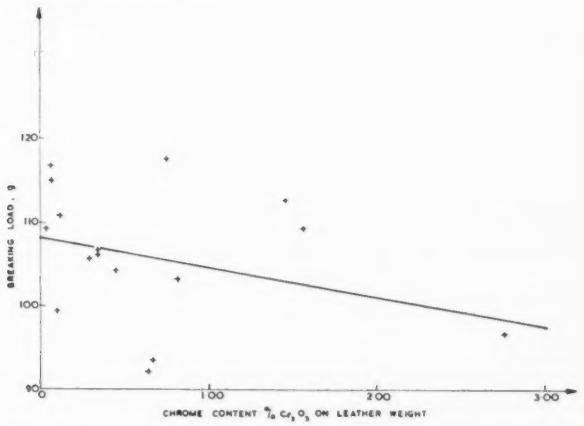

FIGURE 14.—Chrome-tanned fibres. Scatter diagram showing the effect of chrome content on strength.

fibres were tanned the same amount. To check this point chemical analyses were done on the small pieces of pelt tanned with the fibres, sorted for total time in tan. In what follows it is assumed that these pelt analyses are essentially similar to the results that would have been obtained if the fibres had been analysed. This is a reasonable assumption, since the pieces of pelt each weighed less than $\frac{1}{2}$ g., were of a very open texture, and only about 1 mm. thick. The results of the analyses showed that the degree of tannage of the vegetable-tanned fibres ranged from 25% to 95% (average 52%) while the chrome content (as Cr_2O_3) on the leather weight of the chrome-tanned fibres ranged from 0.03% to 2.77% (average 0.66%). Thus the experimental conditions were correctly chosen so that some fibres received a light, and others a heavy, tannage. As shown in Figs. 13 and 14, the strength is almost independent of tan content: fibres heavily tanned have average breaking loads little, if any, different from those lightly tanned (the slight loss of strength which occurs with increasing intensity of tannage in both the vegetable and chrome processes is not significant).

The results for breaking extension were generally similar to those for breaking load, considered above. Hot-pitting reduced the breaking extension of the vegetable-tanned fibres slightly, and fibres hot-pitted for 1 hour, 1 day, and 1 week gave average results of 17.3%, 16.5%, and 15.0% respectively. Fibres not hot-pitted had an average breaking extension of 17.1%. A long vegetable tannage (whether it included a hot-pit stage or not) reduced the average breaking extension; thus Fig. 15 shows that as the total time in tan

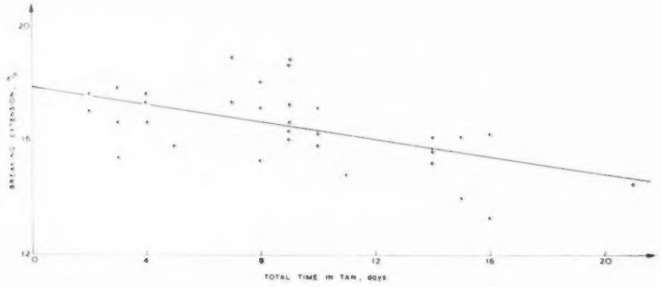

FIGURE 15.—Vegetable-tanned fibres. Effect of total time in tan on breaking extension.

was increased from 2 days to 21 days the average breaking extension fell from 17.5% to 14.6%.

The fact that fibre strength and breaking extension is almost unaffected by changes in processing is of considerable interest, since it means that no serious loss of fibre strength is likely to result from any changes the tanner may normally wish to make in his processing. The wide variations in tensile

strength found with vegetable- and chrome-tanned leathers must therefore be due to changes in fibre weave, orientation, and lubrication rather than to changes in actual fibre strength. Changes of this kind probably permit more uniform distribution of the applied load and hence an increase in leather strength. This emphasises that results obtained on fibres are not necessarily directly applicable to bulk leather and shows that caution is required in interpreting the physical properties of leather from a knowledge of the physical properties of its constituent fibres.

Overall effect of tannage: comparison of the results for raw and tanned fibres.—Changes in processing have little, or no, influence on fibre strength or extensibility. This, however, does not mean that no changes occur during tannage. The overall effect of tannage may be determined by comparing the results obtained in the different experiments discussed here (this comparison is permissible because all the fibres were taken from the same small pieces of pelt and tested under similar conditions).

(*a*) Effect of weight per unit length.—Comparison of the results for raw and tanned fibres on a weight basis gives the curves shown in Figs. 16 and 17. In both these figures the curve representing the results for the raw

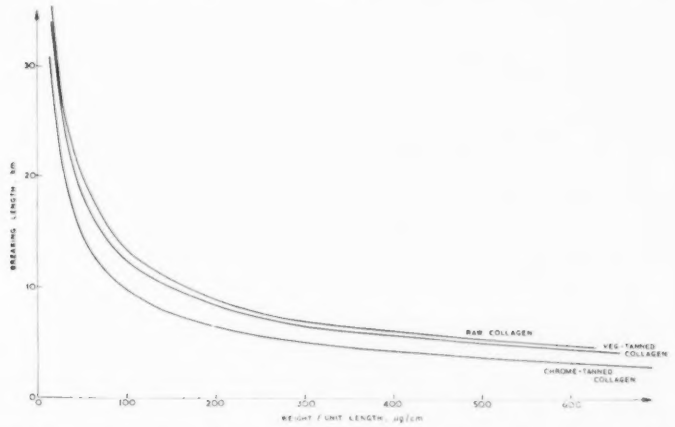

FIGURE 16.—Comparison of raw and tanned fibres: effect of tannage on breaking length, comparison made on a weight basis.

fibres lies above those representing the results for the tanned fibres. Both vegetable and chrome tannage therefore reduce the fibre strength in the sense that a tanned fibre is weaker than a raw fibre with the same weight per unit length. This is shown clearly in Fig. 18, which gives the difference in

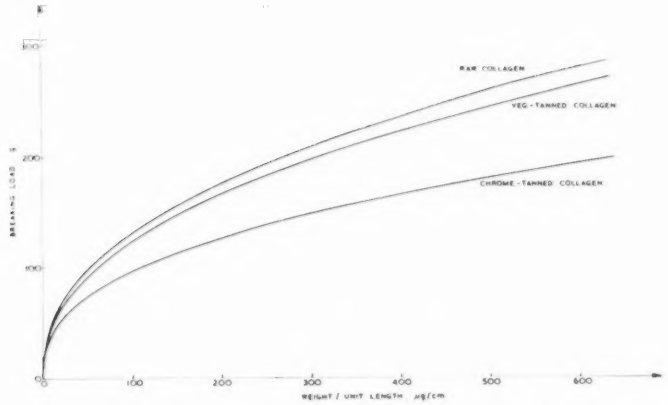

FIGURE 17.—Comparison of raw and tanned fibres: effect of tannage on breaking load comparison made on a weight basis.

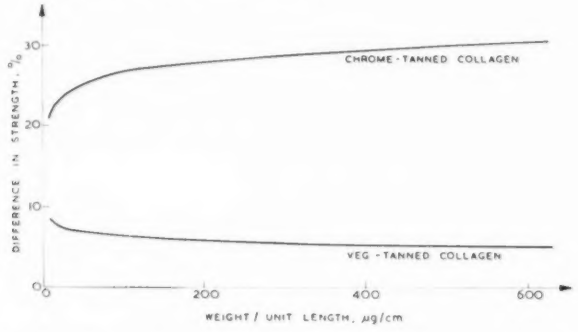

FIGURE 18.—Comparison of raw and tanned fibres: difference in strength plotted against weight per unit length.

strength plotted against weight per unit length: the difference in strength depends somewhat on the weight per unit length, and is about 5% for vegetable-tanned fibres, and 25% for chrome-tanned ones. Tannage also reduces the breaking extension: Fig. 19 shows that the average breaking extension of raw, chrome-tanned, and vegetable-tanned fibres is about 25%, 20%, and 15% respectively. Breaking extension is not very dependent on fibre weight per unit length, except possibly for the lighter vegetable-tanned fibres.

(*b*) Effect of humidity.—The strength and breaking extension of both raw and tanned fibres depends on the humidity at which they were tested. The effect of humidity on breaking length is shown in Fig. 20. Raw and

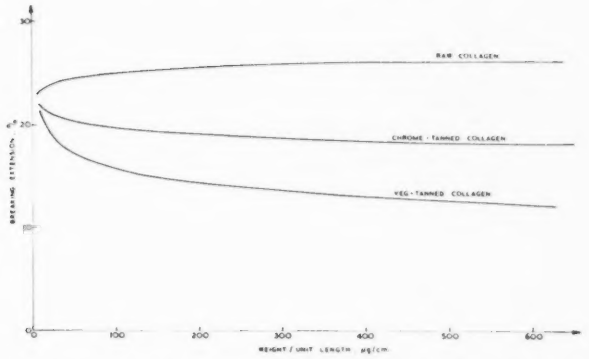

FIGURE 19.—Comparison of raw and tanned fibres: effect of tannage on breaking extension, comparison made on a weight basis.

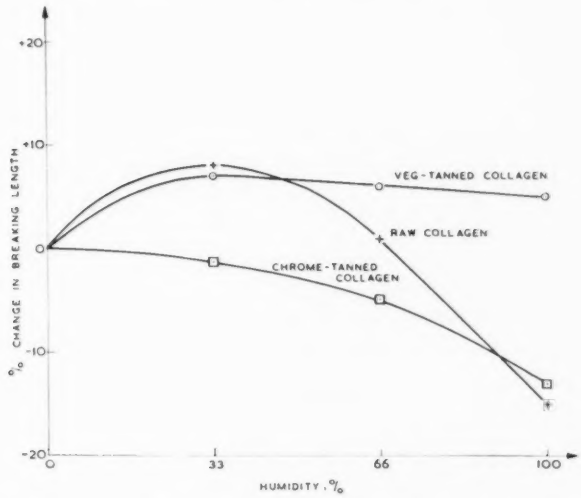

FIGURE 20.—Comparison of raw and tanned fibres: effect of humidity on breaking length of raw and tanned fibres.

vegetable-tanned fibres are strongest at intermediate humidities, and their strengths then decrease as the humidity approaches saturation. Chrome-tanned fibres, on the other hand, are strongest when quite dry, and their strength decreases steadily as the humidity is raised. Figure 21 shows the effect of humidity on breaking extension. This is greater at high humidities than at low for both raw and tanned fibres, but whereas moist vegetable-

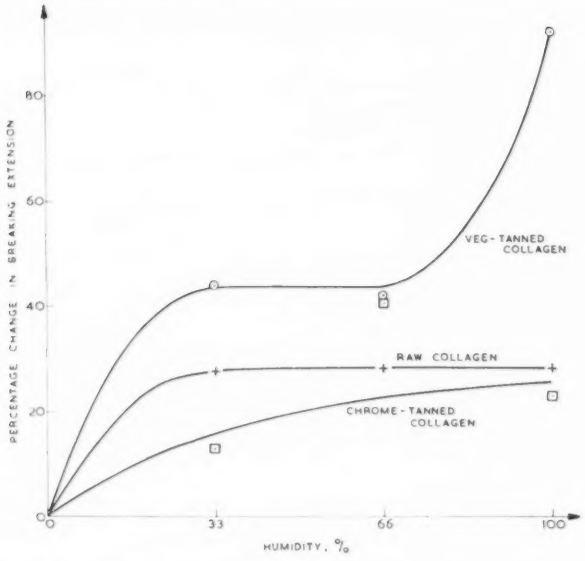

FIGURE 21.—Comparison of raw and tanned fibres: effect of humidity on breaking extension of raw and tanned fibres.

tanned fibres are about twice as extensible as dry, raw and chrome-tanned fibres are only about one quarter more extensible when moist than when dry. The substantial increase in breaking extension shown by the vegetable-tanned fibres between humidities of 70% and 100% is not found for the raw or chrome-tanned fibres because the strength of these drops sufficiently over this range of humidities to keep their breaking extensions almost constant.

CONCLUSION

This paper has described work of a long-term nature which has no direct application in leather manufacture, and for this reason it might be thought that there is little justification for this type of investigation. However, the kind of work described here provides valuable background information which not only serves as a basis for applied research on practical problems but also enables a fuller understanding of some of the processes associated with leather manufacture to be obtained. Further, methods which may lead to a significant improvement in leather quality only become apparent when this kind of information has been obtained. It follows that work of the nature described in this paper has an important part to play in the advance of leather science and is ultimately of very considerable importance to all sections of the leather industry.

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THE INFLUENCE OF HYDROGEN BONDING ON THE SOLVENT DEHYDRATION OF HIDES AND SKINS

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ABSTRACT

When the production of solvent-dehydrated hides is attempted under practical conditions, utilizing previously published information, unexpected difficulties are encountered. These difficulties, localized areas of apparently poor dehydration, make their appearance during the solvent evaporation ("desolventizing") which follows the removal of water by the solvent. They are due to the effects of small quantities of water which are recondensed on the surfaces of the hides by the cooling effect that must accompany the evaporation of the solvent.

The difficulty can be eliminated by the addition of small quantities of solvent-soluble organic materials to the dehydration solvent; these materials protect the stock from condensed water during desolventizing. These materials are effective to the extent that they contain functional groups which have the power to form hydrogen bonds and thus protect the grain surface by a type of "tannage". Alcohols, ethers, glycol ethers, and many other types of compounds are effective for this purpose.

The proposed hydrogen-bonding mechanism was further verified by the ability to develop an empirical formula which permitted the calculation of a quality index for suggested dehydration "additives". The potential effectiveness of untried additives was calculated, predicted, and then verified by experiment.

These results provide a simple and practical solution to a serious practical problem in solvent processing. In addition they provide further experimental verification for previously published ideas on the mechanism of organic tannage, and indicate the possibility that many additional tannages may be achieved in relatively anhydrous systems.

INTRODUCTION

The first suggestions that tanning processes might advantageously be carried out in nonaqueous solvent systems appeared in the literature nearly fifty years ago. Since that time many patents and other publications have described various techniques and potential applications of such systems (1). Until recently these published results were generally based on small-scale laboratory work; the principal emphasis was on the use of solvent-processing techniques to produce leathers practically identical with those produced by conventional aqueous processes. Little mention was made of the underlying mechanisms or other theoretical considerations of solvent processing, and scant attention was given to serious physical and economic problems that would be encountered in any attempt to carry out such processes on a large commercial scale.

In recent years interest in these matters has been greatly intensified in the United States of America. Several groups in the tanning industry have strongly supported research and development programs for the purpose of instituting the solvent processing of hides on a commercial basis (2, 3). This has required a great increase in the scale of the experiments. This fact, coupled with the commercial requirements of a routinely reliable rapid process, a high level of solvent recovery, and a minimum quantity of solvent inventory, has produced some previously unsuspected problems of considerable theoretical and practical interest.

The usual first step in solvent processing is the dehydration of the wet hide, by which is meant the displacement of the water in the hide with a nonaqueous solvent. Commonly this procedure was applied to the wet hide or skin after unhairing. It is generally accomplished by immersion of the stock in a sufficient quantity of an appropriate water-miscible solvent until equilibrium is approached at some desired low level of water concentration.

From this state, variations are possible. One useful procedure is the evaporation of the liquid ("desolventizing") from the stock, which produces solvent-free dehydrated hide substance for subsequent tanning procedures. When carried out under ideal conditions it results in plump, spongy, porous, smooth-textured stock with a pure white grain surface. Such dehydrated stock could be readily tanned in a solvent system (4), or it could be held in ordinary storage indefinitely and then wet back with water for a conventional aqueous tannage.

The proposal has recently been made that the procedure be utilized as a commercial method of curing (5). Such "solvent curing" would be applicable to wet fresh hides, either dehaired or with the hair on; the product would be very stable, elegant raw stock for transportation, storage, and ultimate tannage by aqueous or solvent procedures.

We have carried out considerable experimentation on a pilot-plant scale to study these dehydration and desolventizing operations. Each experiment was performed on several whole hides as a batch. It was noted almost at once that the available published information had not anticipated the conditions that would be encountered even in a modestly sized attempt to operate under approximate practical conditions and quantities. Specifically, on a small percentage of the total surface area, after desolventizing, the grain was yellow and hard, and thus characterized by the effects of what seemed to be poor dehydration.

This effect was not readily reversible; after subsequent tannage it had adversely affected the appearance and properties of the leather in those regions where it was initially observed. It was, therefore, essential to determine the cause of this phenomenon and to propose and develop methods for its elimination without seriously adding to the basic engineering and economic problems of solvent processing.

ANALYSIS OF THE PROBLEM

We were able to demonstrate that the trouble was not due to the dehydration step *per se*—even after the most complete water removal the trouble could be detected on occasion—and it soon became apparent that the desolventizing operation was responsible. During evaporation traces of residual water from the stock, or from the air stream used to carry off the solvent, were condensed on the surface of the stock by the cooling effect of the solvent evaporation; this, in effect, would undo the previous dehydration effort, and the properties of the grain surface at that point would be similar to those of stock that had been dried directly from water.

This effect has been occasionally observed by those engaged in preparation of dehydrated stock for laboratory use. If the stock after prolonged immersion in an excess of relatively pure solvent is simply hung in a room overnight, evaporation of the solvent occurs. During the drying period the relative humidity of the ambient atmosphere may be high enough to produce unsatisfactory results. The cooling at the surface of the hide which is caused by the evaporation will then be accompanied by increased condensation of water at the grain surface, with results as described above. This can, of course, occur to varying degrees, and some of the decreases in grain quality would be rather subtle and difficult to detect by an inexperienced observer, particularly if the stock is not subsequently tanned. Tannage generally makes the defects more clearly apparent to visual examination. To avoid this trouble in laboratory preparations, it is good practice to lay the solvent-soaked stock out on a flat surface and then cover it with thick paper. This acts to slow down the evaporation, which permits the ambient temperature to keep pace better with the evaporative cooling tendency, and it also isolates the stock from moisture condensed from the neighboring atmosphere.

Under practical conditions the time of immersion and the quantities of solvent used in the dehydration are somewhat limited by economic considerations; this also means that the desolventizing operation must be completed in a reasonable time. Therefore, the presence of some residual water and definite evaporative cooling must be considered under practical conditions. Several methods of solving the problem were investigated.

In this paper we shall describe a procedure based on the addition of small quantities of solvent-soluble organic materials to the dehydrating solvent—materials which protected the stock from condensed water during the desolventizing. There appeared to be a consistent mechanism by which these materials (which we have termed "additives") protected the stock. Further investigation showed that the effectiveness of these materials was based on the extent to which they contained functional groups which had the power to form hydrogen bonds. These included compounds which acted either as donors or acceptors of the hydrogen nuclei.

Furthermore, there was an optimum range of hydrogen-bonding power; weaker hydrogen-bonding tendencies were not sufficiently helpful, and very strong hydrogen-bonding tendencies made matters worse, probably because of the added hygroscopic properties which accompanied the increase in hydrogen-bonding ability. The compounds of principal interest were alcohols, ethers, amines, polyglycol ethers, etc., of low molecular weight.

This hypothesis concerning the mechanism of the action of these additives was further verified by the ability to develop an empirical formula which permitted the numerical calculation of a dehydration-quality index for each suggested additive in terms of its functional groups, hydrogen-bonding potential, and molecular-chain length. This index was also used to calculate and predict the prospective effectiveness of untried additives, and in such cases the predicted effects were verified by experimental results.

It is realized that one of the criteria of tannage is the ability of the tanned hide substance to withstand this deleterious action of water on drying. In that sense, these organic additives may be considered tanning materials, although none of the materials described here are ordinarily considered as tanning materials. They are colorless low-molecular-weight materials which can readily be extracted from the hide substance with water or other suitable solvent. In addition to their practical value in this application they are of considerable interest because they represent a relatively rare instance where a mechanism of combination with the hide substance by known, pure molecular species can be systematically calculated and predicted.

METHODS AND COMPOUNDS

In the course of this work several dozen compounds were evaluated for their effectiveness as dehydration aids. Systematic experimental and evaluation procedures were carried out in the laboratory; the most promising materials

were checked under pilot-plant conditions. Since we were most interested in the condition of the grain surface, our results and interpretations were not significantly affected by sampling differences within or between hides. A typical laboratory procedure was as follows:

1. Bated or other wet stock from the tannery was cut into rectangles approximately 18 cm. x 25 cm., and weighing approximately 400–450 g. (about 70% H_2O).
2. The pieces were then soaked in fresh solvent until equilibrium was attained, generally at a water content of less than 10%.
3. Acetone was the principal solvent; results with other useful solvents such as methanol were similar.
4. The solvent-to-wet-stock ratio was generally in excess of 7:1. The additive concentration was generally below 2% of the solvent. Actually, only the final equilibrium concentration of water and the ratio of additive to solvent were important.
5. After immersion and attainment of equilibrium at the desired water concentration, the stock was then desolventized by evaporation in a forced-draught oven; this was generally accomplished in less than one hour.

The evaluation of the quality of the dehydrated stock, while primarily subjective, was consistent. A 10-point quality-rating scale was established, covering the range of *very poor* to *excellent*, in terms of the softness and whiteness of the grain. This was later verified by more exact measurements, including surface hardness, rate of grain rewetting, grain strength (manifested as cracking during tensile testing), and observation of slow penetration and pebbled grain in subsequent tanning and finishing steps.

After early experiments produced a consistency of results based on molecular structure, the concentration of the additive was set on a uniform molal basis, generally at 0.1 gram-mol. of additive per 100 g. of solvent, so that the action of equal numbers of molecules was always being compared.

Because of their practical availability, the initial experiments were carried out with primary alcohols, ethylene glycol monoethers ("cellosolves"), diethylene glycol monoethers ("carbitols"), and miscellaneous other compounds. The final evaluations included amines (considered as the nitrogen analogs of the alcohols and ethers), higher-molecular-weight synthetic waxes, lubricants, and nonionic detergents ("Carbowaxes", "Ucons", "Tergitols", etc.), phenolic compounds, aryl-alkyl compounds, ketones, aldehydes, acids, esters, etc.

RESULTS AND DISCUSSION

The following tentative conclusions were drawn from the initial experiments (*see* Table I):

The additives, to be effective, should have a low vapor pressure at the boiling point (ca. 55°C.) of the dehydration solvent. Therefore, their boiling points should preferably be above 125°–150°C. All other factors being equal, boiling points are a function of the number of carbon atoms in the molecule.

The additives should not be too hygroscopic. Glycerine, ethylene and propylene glycol, ethylene and propylene diamine, diethylene glycol, etc., were all notoriously hygroscopic compounds, and they gave worse results than the controls (no additive).

Additives should possess definite hydrogen-bonding ability. Primary alcohols were effective within certain limits. Monoethers and secondary and tertiary alcohols were generally ineffective. The glycol ethers, within certain limits, were very effective, and this is consistent with their water solubility, which is based on their accumulated hydrogen-bonding ability.

The effectiveness of any particular functional group was further affected by the ratio of such functional groups to the chain length (number of C atoms). The lower-molecular-weight primary alcohols have abnormally high boiling points and are fairly hygroscopic, which is due to their powerful hydrogen-bonding ability. The higher-molecular-weight primary alcohols have nearly normal boiling points and are slightly hygroscopic, indicating weak hydrogen-bonding ability. Their effectiveness as additives is practically parallel, after due allowance for volatility.

We then proceeded to construct an empirical formula which would give due weights to the experimental results listed above and which, for a given class of compounds, used as additives, would properly describe the quality of the dehydration. For aliphatic compounds containing only primary alcohol groups and ether linkages the formula is:

$$N = \frac{400 + 1\frac{1}{2}(a + 1)^4 + 120\,b^2}{n}$$

where

N is defined as the numerical index of dehydration quality,
a is the number of ether (–O–) groups,
b is the number of primary hydroxyl (–OH) groups, and
n is the number of carbon atoms.

The results first noted and further experiments indicated that there is an optimum range where $N = 60$ to 80 (*see* Fig. 1). Below 50 the compound possesses very weak hydrogen-bonding ability. Above 90 the compound is

TABLE I

CHARACTERISTICS OF VARIOUS ADDITIVES

Additive	Formula	B.Pt.(°C.)	Dehydration Quality
None (Control)	—	—	Poor
Dioxane	$-CH_2-CH_2-O-CH_2-CH_2O-$	101	Poor
Dibutyl ether	$C_4H_9-O-C_4H_9$	142	Poor
n-Hexanol	$CH_3(-CH_2)_5-OH$	157	Fair
Di-isobutyl carbinol	$C_4H_9-CHOH-C_4H_9$	178	Fair
Glycerine	$CH_2OH-CHOH-CH_2-OH$	290	Very poor
Butyl carbitol	$C_4H_9(-O-CH_2-CH_2)_2-OH$	231	Excellent
Diethylene glycol	$CH_2OH-CH_2-O-CH_2-CH_2OH$	246	Poor
Polyalkylene glycol	"Tergitol NP-27"–	—	Very good
Propylene glycol	$CH_3-CHOH-CH_2OH$	187	Poor
2-ethyl hexanol	$CH_3\ (-CH_2)_3-CH(C_2H_5)-CH_2OH$	185	Good–Very good
2-ethylhexylamine	$CH_3\ (-CH_2)_3-CH(C_2H_5)-CH_2NH_2$	169	Good
Triethylene tetramine	$NH_2(-CH_2-CH_2-NH)_2-CH_2-CH_2-NH_2$	277	Poor–Fair
n-Octanol	$C_7H_{16}-CH_2-OH$	195	Good

TABLE II

COMPARISON OF CALCULATED EFFECTS OF ADDITIVES WITH OBSERVED EFFECTS

Additive	B.Pt. (°C.)	Formula	Calc. Index	Dehydration Quality (Observed)
n-Dodecanol	255	$CH_3(-CH_2)_{10}-CH_2-OH$	43	Poor–Fair (3)
Dibutyl ether	142	$C_4H_9-O-C_4H_9$	51	Poor (2)
n-Decanol	231	$CH_3(-CH_2)_8-CH_2-OH$	52	Fair (4)
Vinyl butyl cellosolve	—	$CH_2=CH-O-CH_2-CH_2-O-C_4H_9$	55	Fair–Poor (3)
Hexyl carbitol	259	$C_6H_{13}(-O-CH_2-CH_2)_2-OH$	56	Good (6)
Dibutoxy tetraglycol	335	$C_4H_9(-O-CH_2-CH_2)_4-O\ C_4H_9$	65.5	Very good (9)
Hexyl cellosolve	208	$C_6H_{13}-O-CH_2-CH_2-OH$	66	Very good (8)
Diethyl carbitol	188	$C_2H_5(-O-CH_2-CH_2)_2-O-C_2H_5$	66	Very good (9)
Ethoxy triglycol	255	$C_2H_5(-O-CH_2-CH_2)_3-OH$	81	Good (7)
Butyl cellosolve	171	$C_4H_9-O-CH_2-CH_2-OH$	88	Fair (4)

TABLE III

RELATIONSHIP OF MOLECULAR STRUCTURE TO THE USEFULNESS OF ADDITIVES

Group	Additive	B.Pt. (°C.)	Structural Formula	Groups (OH)	Groups (-O-)	Groups (C)	Quality	Index (N)
A	Methyl cellosolve	125	CH_3-O-CH_2-CH_2-OH	1	1	3	Poor (2)	176
	Ethyl cellosolve 1	135	C_2H_5-O-CH_2-CH_2-OH	1	1	4	Poor (2)	132
	Butyl cellosolve	171	C_4H_9-O-CH_2-CH_2-OH	1	1	6	Fair (4)	38
	Hexyl cellosolve	208	C_6H_{13}-O-CH_2-CH_2-OH	1	1	8	Very good (8)	66
B	Methyl carbitol	194	CH_3-O-CH_2-CH_2-O-CH_2-CH_2-OH	1	2	5	Poor (2)	112
	Ethyl carbitol	195	C_2H_5-O-CH_2-CH_2-O-CH_2-CH_2-OH	1	2	6	Poor-Fair (3)	93
	Butyl carbitol	231	C_4H_9-O-CH_2-CH_2-O-CH_2-CH_2-OH	1	2	8	Excellent (10)	70
	Hexyl carbitol	259	C_6H_{13}-O-CH_2-CH_2-O-CH_2-CH_2-OH	1	2	10	Good (6)	56
C	n-Hexanol	157	CH_3-$(CH_2)_4$-CH_2-OH	1	0	6	Fair (4)	87
	n-Heptanol	176	CH_3-$(CH_2)_5$-CH_2-OH	1	0	7	Very good (8)	74.5
	n-Octanol	195	CH_3-$(CH_2)_6$-CH_2-OH	1	0	8	Good (6)	65
	n-Nonanol	213	CH_3-$(CH_2)_7$-CH_2-OH	1	0	9	Fair-Good (5)	58
	n-Decanol	231	CH_3-$(CH_2)_8$-CH_2-OH	1	0	10	Fair (4)	52
	n-Dodecanol	255	CH_3-$(CH_2)_{10}$-CH_2-OH	1	0	12	Poor-Fair (3)	43
D	Dibutyl ether	142	C_4H_9-O-C_4H_9	0	1	8	Poor (2)	51
	Dioxane	101	CH_2-CH_2-O-CH_2-CH_2-O-	0	2	4	Poor (2)	110
	Vinyl butyl cellosolve	–	CH_2=CH-O-CH_2-CH_2-O-C_4H_9	0	2	8	Poor-Fair (3)	55
	Dibutyl cellosolve	204	C_4H_9-O-CH_2-CH_2-O-C_4H_9	0	2	10	Poor-Fair (3)	44
	Diethyl carbitol	188	C_2H_5-O-CH_2-CH_2-O-CH_2-CH_2-O-C_2H_5	0	3	8	Very good (9)	66
	Dibutoxy tetraglycol	335	$C_4H_9(-O-CH_2-CH_2)_4-O-C_4H_9$	0	5	16	Very good (9)	65.5
	Dibutyl carbitol	255	$C_4H_9(-O-CH_2-CH_2)_2-O-C_4H_9$	0	3	12	Poor-Fair (3)	44
E	n-Octanol	195	CH_3-$(CH_2)_6$-CH_2-OH	1	0	8	Good (6)	65
	Hexyl cellosolve	208	C_6H_{13}-O-CH_2-CH_2-OH	1	1	8	Very good (8)	66
	Butyl carbitol	231	$C_4H_9(-O-CH_2-CH_2)_2-OH$	1	2	8	Excellent (10)	70
	Ethoxy triglycol	255	$C_2H_5(-O-CH_2-CH_2)_3-OH$	1	3	8	Good (7)	81

TABLE IV

PROPERTIES OF ADDITIVES CONTAINING AROMATIC GROUPS AND VARIOUS OTHER FUNCTIONAL GROUPS

Group	Additive	Structural Formula	Dehydration Quality	
F	Phenol	C_6H_5-OH	Good	(6)
	Cresol	$C_6H_4(CH_3)-OH$	Good	(6)
	p-isopropyl phenol	$(CH_3-)_2CH-C_6H_4-OH$	Fair–Good	(5)
	p-phenyl phenol	$C_6H_5C_6H_4-OH$	Fair	(4)
G	p-methyl benzaldehyde	$CH_3-C_6H_4-CHO$	Fair–Good	(5)
	p-methoxy benzaldehyde	$CH_3-O-C_6H_4-CHO$	Good	(6)
	p-methyl benzoic acid	$CH_3-C_6H_4-COOH$	Good	(6)
	p-methoxy benzoic acid	$CH_3-O-C_6H_4-COOH$	Good	(6)
	p-methoxy benzyl alcohol	$CH_3-O-C_6H_4-CH_2OH$	Good–Very good	(7)
H	Phenyl ethyl alcohol	$C_6H_5-CH_2-CH_2-OH$	Good–Very good	(7)
	2-ethyl hexanol	$CH_3(-CH_2)_3-CH(-C_2H_5)-CH_2-OH$	Good–Very good	(7)
	2-ethyl hexanoic acid	$CH_3(-CH_2)_3-CH(-C_2H_5)-COOH$	Good	(6)
	2-ethyl hexaldehyde	$CH_3(-CH_2)_3-CH(-C_2H_5)-CHO$	Poor	(2)
	2-ethyl hexyl amine	$CH_3(-CH_2)_3-CH(-C_2H_5)-CH_2NH_2$	Good	(6)
	2-ethyl hexyl chloride	$CH_3(-CH_2)_3-CH(-C_2H_5)-CH_2CL$	Fair–Good	(5)
J	Butyl carbitol acetate	$C_4H_9(-O-CH_2-CH_2)_2-O-COCH_3$	Poor–Fair	(3)
	Ethyl cellosolve acetate (B.Pt.156°C.)	$C_2H_5-O-CH_2-CH_2-O-COCH_3$	Fair	(4)
	Acetophenone	$C_6H_5-CO-CH_3$	Poor–Fair	(3)
	Diethoxy tetrahydro furan	$CH_3-CH_2-O-HC(-O-CH-O-CH_2-CH_2)-H_2C-CH_2$	Poor	(2)

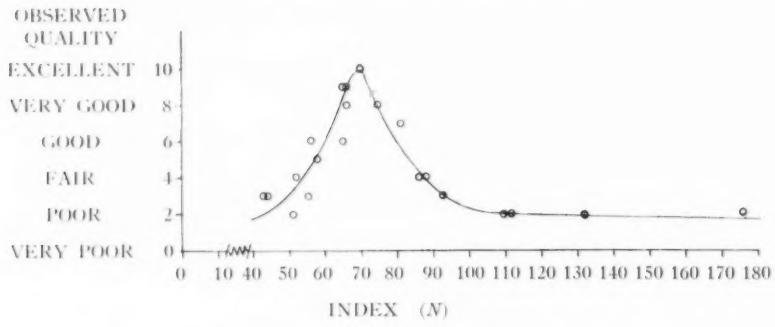

FIGURE 1.—Quality versus Index (N). Compounds in Table III.

either too volatile or too hygrocsopic. The formula, by means of the coefficient of the b term, initially provides relatively greater weights to the stronger hydrogen-bonding ability of primary hydroxyl groups; it provides by means of the exponent in the a term for the cumulative effect of multiple ether groups; a volatile material (low value of n) will cause the index to increase beyond the optimum range. The peak value on the curve ($N = 70$) is produced by "butyl carbitol" (diethylene glycol monobutyl ether) and this is a preferred additive in practice.

The formula applies directly only to alcohols, ether alcohols, and ethers. Secondary alcohol groups could be covered by an additional term in the numerator, but its magnitude in relation to the other terms would be small. This was experimentally verified by the almost identical results obtained with 2-ethyl hexanol-1 and 2-ethyl hexanediol-1,3. Presumably, analogous formulae could be constructed for other families of compounds.

A further test of the applicability of the mechanism and formula was made by selecting certain compounds in this group covering a wide range of molecular-weight and functional-group totals. The quality indices (N values) were calculated for these compounds. Dehydrated stock was then prepared using these compounds as additives, and the quality of the dehydration was compared with the predicted calculated values. These results are listed in Table II, and the results are included in the plot in Fig. 1, where they fall properly on the curve.

The consistency and broad coverage of the formula is illustrated by Table III. The compounds are listed in systematic order on the basis of their functional groups; the increase, peak, and decline of dehydration quality and the corresponding N value are illustrated for each group of compounds. Group A shows the progression of properties with increasing n for constant values of a and b. Decreasing volatility and decreasing hygroscopicity cause

a decrease of N, from too high initial values down to the proper range. Groups B and C are similar, but with still further increased n the quality declines further, ultimately below the optimum range. Group D contains examples of high volatility (dioxane), weak hydrogen bonding (dibutyl ether, vinyl butyl cellosolve, dibutyl cellosolve, and dibutyl carbitol), and the cumulative effect of multiple ether groups on a relatively large chain length (dibutoxy tetraglycol). Group E illustrates the progression of properties for a constant carbon number but with an increasing number of ether linkages, finally resulting in a fairly hygroscopic compound (ethoxy triglycol).

Many other classes of organic compounds were also evaluated. These results are partially tabulated in Table IV. Again the pattern is consistent with hydrogen-bonding ability. This is illustrated in Group G by the effects of the aliphatic oxy and alcohol groups and by the correlation of quality with the superior hydrogen-bonding ability of the benzoic acid in contrast to the benzaldehyde. These relative effects are also illustrated in Group H. This group is of further interest in that the 2-ethylhexyl chloride is poorer, as expected; the 2-ethylhexylamine is better, again as expected. Group J illustrates the sharp reduction in the effectiveness of butyl carbitol when its primary alcohol group is replaced by the ester group, with consequent reduction of hydrogen-bonding ability. On the other hand the relatively volatile and hygroscopic ethyl cellosolve (*see* Group A, Table III) is improved by the substitution of the ester group for the hydroxyl group.

Group F in Table IV illustrates the relative effectiveness of the phenolic hydroxyl groups. The lack of effectiveness of acetophenone is in keeping with its low hydrogen-bonding ability. Diethoxy tetrahydrofuran has a favorable ratio of oxy groups to carbon atoms, but the ring oxygen and the side chain oxygen are separated by only one C atom; accordingly, the properties of these oxy groups probably differ from those of the glycol ethers.

CONCLUSIONS

Thus it can be seen that a very wide range of organic compounds possess "tanning" properties which they can exercise under relatively anhydrous conditions. This should have interesting implications in future investigations of new tannages in solvent systems. The broad mechanism of the action of these compounds can be consistently predicted in terms of the hydrogen-bonding ability of the compounds. This is consistent with the published literature on the mechanisms of organic tannage, collagen structure, bound water, etc. (6)

The process by which these compounds produce their effect can probably be postulated in several ways. The fact that there is an optimum range of hydrogen-bonding ability for these additives commands special attention. If the shrinkage and adhesion which occur as collagen is dried from water are assumed to be caused by formation of a strong hydrogen bond and possible

other linkages between adjacent chains as the water is removed, these materials apparently act to prevent this. The mass action effect of the dehydration solvent has already ruptured the linkages of water to chain, and water to water, in the wet stock, and these materials by themselves entering into combination with the chains may act to block the shrinkage and adhesion on drying. Materials which have too much hydrogen-bonding ability, or residual ability after such primary combination, can retain and even capture water with adverse results.

It should be finally noted th. .he effectiveness of these materials increases with increasing concentration this permits acceptably dehydrated stock to be produced at higher concentrations of water in the final solvent mixture. At higher water concentrations and less than 100% equilibrium these materials in sufficient concentration will offer adequate protection to the interior fibers as well as the grain surface. This permits the production of excellent dehydrated stock under conditions of time and concentration that have considerable added practical value. This increased knowledge of the physical and chemical mechanisms involved in the dehydration and desolventizing steps can add substantially to the confidence and expectations attendant upon modernization of hide processing through solvent procedures.

ACKNOWLEDGMENTS

The support and interest of the tanners who comprise the Leather Research Corporation are sincerely acknowledged. We also wish to acknowledge the very tangible assistance rendered by Mr. R. Gene Kelso and the Carbide & Carbon Chemicals Corporation for their efforts in supplying experimental quantities of many of the compounds herein described.

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DISCUSSION

CARL TELANDER: It is quite a treat to have a paper on this intriguing subject presented to us, and it is even more of a treat to have something so new and revolutionizing revealed to us. We are indeed indebted to Dr.

Kremen and Mr. Southwood for removing this first veil of secrecy from this subject. By the time the seventh and final veil falls I hope the beautiful subject will be revealed to us in its completeness.

I know from personal experience in the days when I was actively engaged in this subject and its development how important this discovery of Dr. Kremen's was. I don't know if he has sufficiently stressed to you the importance of it; it actually meant the difference between success and failure.

Whether we agree with Dr. Kremen that the phenomena reported here are true hydrogen bondings or not is of little importance; and whether we can actually ascribe tanning effects to them is also of little importance. What we have here really is a fine piece of research conducted with skill and patience of the highest order. It is to be hoped that it will soon be followed by more reports of the same caliber so that we may finally gain a full picture of this most important and promising field—solvent dehydration in tanning.

DR. BUECHLER: I too want to congratulate Dr. Kremen. As Mr. Telander has pointed out, in any commercial solvent-tanning process, being able to prevent this trouble during desolventizing is the real difference between a commercial working process and a laboratory curiosity. This is why Dr. Kremen has obviously spent a great deal of effort on it. We too, even though we did not always dry from solvent, ran into this same phenomenon. We found, in fact, that even agitating the hides as we did in the presence of air gave a similar effect. As a matter of fact we came up with a working hypothesis also.

In my paper last year, because of the large scope of that paper and the limits of time, perhaps I did not discuss in sufficient detail the problems which Dr. Kremen has discussed here. However, we did experience them, and I am sure others who try to tan in the solvent will experience them.

We came to the conclusion that the reason for the desolventizing difficulty is that as the acetone or other volatile solvent evaporates condensation occurs, as Dr. Kremen has pointed out. But the amount of condensation is not particularly great, and by itself it would not be particularly important. The important thing is that the hide substance is very low in bound water at the point where this occurs. And what you have is a rebinding of that water with the evolution of a great deal of heat. Studies of the rehydration of hide powder have been done by Mitton and Mawhinney in England and by Dr. Kanagy here in this country. Both observers have come to the conclusion that the heat of wetting is 36 calories per gram, which is a tremendous figure; and this heat, as it is evolved, gelatinizes the collagen, particularly at the surfaces. And because of this the later penetration of tannin solutions and of fixing bath—as Dr. Kremen pointed out—is delayed and gives difficulty. The hydrogen-bonding mechanism which he proposes is one way to slow the resorption and recombination with water. There are other methods of doing

this. Any method which will slow that recombination will be effective. And it takes a little work to find one. He has done a great deal of work for which he is indeed to be congratulated.

DR. EDWARD M. FILACHIONE (Eastern Regional Research Laboratory): I have wondered why methanol is not given more serious consideration in this solvent dehydration. It is considerably less expensive.

DR. KREMEN: I would say this: As far as using methanol is concerned, I should have said that we conducted experiments where we used methanol as a solvent. You still have to use an additive, and you get essentially similar results. If we could not get acetone, or if the price differential was right, we could operate with methanol as a dehydration solvent. We were thinking of the subsequent vegetable tannage and did not want to use two solvents, and acetone is better for quebracho than methanol. That is probably the main reason we used it.

Of course, as to the first cost of a solvent, if you have a good recovery and it is 5½ cents for methanol and 8½ cents for acetone, the differential in first cost is not prohibitive, and if your replacement need is relatively low, it is not critical. Both of them cost the same to distill, and they have nearly the same boiling points. The main reason for our choice was that we wanted to use the same solvent for dehydration and tanning. But you would get the same results that I have described here, with methanol.

DR. ANDREW SALAMATOV (Barrett & Co., Inc.): I wonder what happens to the natural grease during this solvent dehydration. Is it completely removed, modified, or what happens to it?

DR. KREMEN: We can answer it in two ways. Almost all of it is taken out, I would say. It depends on whether you get the hide in the fresh condition or whether it has been beamed—because there has been some action on the grease at that point. If the hides have been fleshed, a lot of the grease is gone. But if you are talking about grease among the fibers, the answer is practically all of it, as far as we can tell—85% at least, depending on how you define grease. Some of these greases may be combined or partly combined and could only be removed by hydrolysis. But in any event, at least 85% is taken out. We can verify it by extractive procedures and analyzing for hide substances.

The first dehydrated hide which I showed you, would analyze, on a dry basis, 99% hide substance with a trace of ash, if we first carefully delimed it.

DR. HAROLD D. TURLEY (Rohm & Haas Co.): Dr. Kremen, does this process you have described on a laboratory scale parallel the practical process that you are using?

DR. KREMEN: You mean the method of drying?

DR. TURLEY: Yes.

DR. KREMEN: As Dr. Buechler says, there are several ways. This is one way we have used to make a great deal of better leather. It would be an economic question whether this or some other solution would be used. We think this is economical; however, we also feel that there are other methods that may be as attractive. But this process does give you, certainly initially, a degree of assurance and reproducibility which is very nice to have at the start. The major extra cost involved is the cost of recovering the additive from the still bottoms, which is not prohibitive—plus whatever remains in the hide after you have dried off the acetone. If the hide contained 30 or 40 pounds of acetone, and you are using additive at a 2% level, you have between a half pound and a pound of this material per hide which is lost. So it is not a serious economic problem fortunately. I would say this is one commercial procedure that could be offered, yes.

DR. TURLEY: This is in the closed system?

DR. KREMEN: Yes.

DR. TURLEY: It seems to me that when you get equilibrium and no moisture, then there isn't any problem.

DR. KREMEN: Do you realize the problem of attaining acetone with zero water, even with a countercurrent? Take a simple case: Say a bated hide contains 50 pounds of water. To get down to 5% water and 95% acetone without using a countercurrent, you would have to use 950 pounds of acetone. With a thousand hides daily, nearly 1,000,000 pounds of acetone would have to be handled. If you want to take the final equilibrium to levels of between 95 and 99 acetone, the problem reaches almost fantastic amounts of solvent. Therefore, I think that for an economic solution you will have to figure on living with a small amount of residual water under practical conditions.

DR. TURLEY: Then you would surely have problems later on if you had hides with different amounts of water when you came to rehydrate them, and in tanning.

DR. KREMEN: Put it this way: If you use the additive or one of these other methods and run a routine process, and you run it on a safe or conservative basis and leave it in long enough so that you are assured of equilibrium, you carry your final equilibrium level to a safe point, either with the additive or other procedure.

As to the hides themselves, after they have been dehydrated and desolventized, they will be at a temperature close to the boiling point of the dehydration solvent when removed from the system and allowed to cool down.

As Dr. Buechler has indicated, you will have very little water in the hides at all at that point, regardless of the final equilibrium level. The only moisture will be gained from the ambient humidity in storage. The hides as they come out of the treating system after being desolventized are nearly bone-dry. You have almost an oven-drying effect at the end, because when almost all the solvent is gone the temperature all through the hide and at the surface approaches the boiling point of the solvent—something like 55°C. Later the hides will pick up moisture to a range of 10% or 12%, as any other leather or hide product will do.

Therefore, we do not anticipate trouble at that point. As long as you carry out the dehydration and desolventizing with plenty of margin, then the rest of it takes care of itself.

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—*Science Information News*, June-July, 1959. National Science Foundation, Washington, D. C.

SAMPLING OF SOLE LEATHER

COMMITTEE STUDY OF AREA VS. WEIGHT BASIS FOR COMPOSITING

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ABSTRACT

A study conducted by the ALCA Standards and Specifications Committee indicates that sole leather should be sampled on an equal-area basis rather than on an equal-weight basis.

During preparation of the latest revision of Official Method B1 for sampling sole leather for analysis, C. G. Telander raised a question regarding the method of compositing three pieces from different locations on a back or bend to form a sample for chemical analysis. The point in question was whether the pieces should be of equal weight or of equal area.

The sampling method for sole leather is based upon a committee report prepared by Chairman F. H. Small (1). The provisional method as outlined on page B-2 of the Methods Book published in 1938 required a composite sample of equal weights from each of three locations. This procedure was changed in a revision adopted in 1942 (without reference to further committee work) to require a composite sample of three pieces of equal area (2).

In 1955 the Standards and Specifications Committee began a study of the question of weight vs. area basis for the composite sample of sole leather. An examination of the 1921 committee report revealed that the original results were based upon averages of the composition in different areas without adjusting the size or weight of the pieces. The percent composition in each location was, of course, computed on a weight basis; therefore, the average of the results for any three locations was equivalent to that of a composite sample made up of equal weights from each location.

Although the report by F. H. Small made no comparison of different composite samples, it did include the weights and areas of the pieces which enabled J. R. Kanagy, assisted by J. H. Davis and R. Oehler, to make a direct comparison of results composited on either an area or weight basis. The sample locations for bends A, B, and J were represented by pieces

numbered 26, 5, and 36 in the F. H. Small report, p. 414. The results of the calculations are summarized in Table I. The data show surprisingly close agreement between the results on a weight basis and those on an area basis.

TABLE I

CHEMICAL ANALYSIS OF SOLE LEATHER, 1921
(*% DRY BASIS*)

Basis of Composite Sample	Oil	Ash	Epsom Salt	Sugars	Non-tannins	Tannins	Hide Substance
Weight	2.99	2.17	5.06	3.72	14.54	13.63	33.97
Area	2.99	2.18	5.05	3.74	14.54	13.65	33.99

The study of J. R. Kanagy also included sole leather bends from current production of two different tanners from which composite samples were prepared on both area and weight bases. These results are summarized in Table II.

TABLE II

CHEMICAL ANALYSIS OF SOLE LEATHER, CURRENT PRODUCTION
(*% DRY BASIS*)

Tanner	Basis of Composite Sample	Oil	Ash	Water Solubles	Hide Substance
I	Weight	6.02	4.26	25.85	39.13
	Area	6.07	4.33	26.04	39.12
II	Weight	3.64	6.45	32.76	37.19
	Area	3.53	6.32	32.39	37.30

The agreement between weight and area samples is not as good as in Table I, but all deviations are relatively small. The largest difference, 0.37% for water solubles of Tannage II, is not considered significant.

Because of the surprisingly small difference revealed in these two tables, an additional independent comparison of area and weight samples was made by A. N. Kay on crops of sole leather where locations A, C, and J were substituted for locations A, B, and J in accordance with the provisional sampling method. The results of the chemical analysis were composited on area and weight bases, and the differences in percent for each constituent were calculated, as shown in Table III.

TABLE III

CHEMICAL ANALYSIS OF CROPS
(%, *DRY BASIS*)

	Sample Location			Composite on		
	A*	C*	J*	Area Basis	Weight Basis	Difference
Oil	4.96	5.55	4.79	5.10	5.10	.00
Hide substance	40.30	36.76	35.56	37.70	37.54	.16
Insoluble ash	.06	.08	.08	.07	.07	.00
Water solubles	25.99	28.80	31.86	28.69	28.88	.19
Soluble nontannin	14.01	16.15	17.38	15.73	15.85	.12
Soluble tannin	11.98	12.65	14.48	12.96	13.03	.07
Combined tannin	28.69	28.81	27.71	28.44	28.41	.03
Total ash	3.79	4.55	4.94	4.39	4.43	.04
Glucose	5.17	6.25	6.56	5.95	5.99	.04
Epsom salts	5.50	6.65	6.79	6.27	6.31	.04
Degree of tannage	71.2	78.4	77.9	75.4	75.7	.3

*Sample weight: A, 152.0 g.; C, 134.7 g.; J, 125.1 g.

The differences due to the method of forming the composite sample were of about the same order of magnitude as those reported in Table II. The largest difference found for any constituent was 0.19% for water solubles, which is not considered significant. The difference in degree of tannage was 0.3%, but this also is considered insignificant. The degree of tannage is subject to

TABLE IV

ANALYSIS OF LIGHT AND HEAVY BACKS
(%, *AS RECEIVED*)

	Light*	Heavy*	Composite on		
			Area Basis	Weight Basis	Difference
Moisture	10.97	11.25	11.13	11.11	.02
Oil	5.57	5.80	5.70	5.68	.02
Ash	5.97	4.66	5.22	5.32	.10
Insoluble ash	.16	.13	.14	.14	.00
Epsom salts	9.96	7.26	8.41	8.61	.20
Sugar	9.65	9.00	9.28	9.32	.04
Hide substance	29.78	33.43	31.88	31.60	.28
Water solubles	30.57	26.30	28.11	28.44	.33
Nontannin	22.92	18.74	20.52	20.83	.31
Uncombined tannin	7.65	7.56	7.60	7.60	.00
Combined tannin	22.95	23.09	23.03	23.02	.01
Degree of tannage	77.1	69.1	72.5	73.1	.6

*Sample weight: light, 62 g.; heavy, 84 g.

relatively large variations because it is affected by the accumulation of errors in the analysis.

The effect of wide variations in weight of hides in the same lot on the composite analyses was studied by C. G. Telander. He prepared die-cut specimens from A, C, and J locations of light and heavy backs from the same lot and made the chemical analyses reported in Table IV. The table includes the average composition of light and heavy backs as well as the composite samples.

It is apparent that the variation in weight of the hides in a lot makes only small differences in the composite samples on an area or weight basis, the largest difference being 0.33% for water solubles. The difference for degree of tannage is 0.6%, but as in Table III, this is considered small in comparison with the usual experimental errors inherent in the test methods.

In this paper a different approach to the problem of sampling sole leather is described. An attempt is made to determine the size of the largest difference that might be expected between samples composited on a weight or area basis by an analysis of the factors involved.

First, in order to aid in visualizing the factors that might affect the difference between area and weight averages, the following equation was developed:

$$E = d_1 (p_1 - p_3) + d_2 (p_2 - p_3) \qquad \text{Equation (1)}$$

where

E is the error or difference in percent between the composite analysis on an area basis and that on a weight basis;

p is the percentage composition at any location (A, B, etc.), p_1 being the largest and p_3 the smallest of the three values for any constituent;

d is the deviation in the weight of a specimen from the average, expressed as a fraction of the total sample weight, d_1 corresponding to specimen of composition p_1, d_2 to p_2 and d_3 to p_3.

Equation 1 may be applied to calculate the difference between area and weight values of any constituent, for example, for hide substance in Table III. The computation is as follows:

Specimen	Location	Specimen Weight, g.	p, %
1	A	152.0	40.30
2	C	134.7	36.76
3	J	125.1	35.56
	Total	411.8	112.62
	Average	137.3	37.54

and

Location	Deviation
A	$d_1 = \frac{152.0 - 137.3}{411.8} = 0.0358$
C	$d_2 = \frac{134.7 - 137.3}{411.8} = -0.6200$

Then the difference between area and weight averages is

$$E = 0.0358\ (40.30 - 35.56) - 0.0062\ (36.76 - 35.56) = 0.16\%$$

and the composite value on an area basis is

$$37.54 + 0.16 = 37.70\%$$

which is the same as the value found in Table III.

In equation 1 the difference between the largest and smallest percentage values, p_1 minus p_3, is generally referred to as the range R. In order to simplify the equation, the quantity p_2 minus p_3 will be referred to as S. It may be observed that as p_2 decreases S approaches zero, and as p_2 increases S approaches but never exceeds R. The substitution of R and S in equation 1 gives

$$E = d_1R + d_2S \qquad (2)$$

Since R is generally larger than S and never smaller, the value of E will be greater when d_1 is larger than d_2.

The specimen weight deviations d are related as follows:

$$d_1 + d_2 + d_3 = 0 \qquad (3)$$

which may be written:

$$d_1 = -(d_2 + d_3) \qquad (4)$$

This indicates that for deviations within a given weight range, the maximum value of d_1 is equal to and opposite in sign to the sum of d_2 and d_3. It is also possible that either d_2 or d_3 may be equal to 0.

It should be observed that both R and S in equation 2 are always positive values and that when d_1 has a maximum positive value, d_2 is either negative or equal to 0. Under these conditions the maximum value of E is:

$$E = d_1R + 0 \qquad (5)$$

Although equation 3 shows the relationship among the weight deviations, it gives no clue as to the size of the weight deviations that might be expected in regular production. More definite information on these weight deviations for locations A, B, and J was found in the F. H. Small report and in the study by J. R. Kanagy. The heaviest of the three specimens in the F. H. Small report weighed 23% more than the lightest. In the bends from current production, the heaviest specimen weighed 22% more than the lightest. The relative weights will vary in different hides, but by applying a factor of 2 to the observed values, it may be estimated that the heaviest of the three specimens from a commercial bend will not outweigh the lightest by more than 50%. For the present, it is assumed that the middle specimen weight will be the average of the heaviest and lightest weights as follows:

Specimen	Weight, units
w_1, heaviest	150
w_2, middle	125
w_3, lightest	100
Total	375

The weight of the middle specimen was set equal to the average in order to make the deviation d_2 equal to 0; therefore

$$d_1 = \frac{150 - 125}{375} = .0667$$

$$d_2 = \frac{125 - 125}{375} = 0$$

$$d_3 = \frac{100 - 125}{375} = -.0667$$

Under the conditions described above and with the aid of equation 5, the estimated maximum deviation between weight and area samples is:

$$E = .0667\ R\% \qquad (6)$$

This equation can be used to calculate the maximum deviation to be expected for any component for which R is known.

The chemical compositions of various sole leathers are given in an investigation of the wearing quality of 20 U.S. sole leathers in the so-called Camp Lee Test (3). The figures for water solubles in Table IV of this study show that the average range for all three locations was 6.4%. For any single tannage the maximum range was 11.5% (Tannage U). For hide substance the average range was 4.5%, and the maximum range for any single tannage was 9.2% (again Tannage U). From these values the maximum E values are computed, as shown in Table V. The results indicate that E does not exceed the usual experimental errors in these tests.

TABLE V

DIFFERENCE E BETWEEN RESULTS OF "CAMP LEE TEST" ON AREA VS. WEIGHT BASIS

Component	Range R, %	Area vs. Weight Deviation E, %
Water solubles, average	6.4	0.43
Water solubles, maximum	11.5	0.77
Hide substance, average	4.5	0.30
Hide substance, maximum	9.2	0.61

The preceding analysis has been restricted to conditions under which the average range R is relatively large on the assumption that the value for S of equation 2 would be much smaller and would have little effect on E. In order to cover more general cases, information is required on the values of R and S in commercial production. The values of S can also be obtained from the above-mentioned Camp Lee Test (3). For water solubles the average value of S was 3.0%; the average value for any single tannage was 5.4% (Tannage U). In each case the value of S proved to be slightly less than half as large as the R values mentioned earlier.

TABLE VI

SPECIMEN WEIGHT DEVIATIONS FROM AVERAGE WEIGHT

Middle Specimen Weight, w_2	d_1	d_2	d_3
100	.0952	−.0476	−.0476
110	.0833	−.0278	−.0556
120	.0721	−.0090	−.0631
125	.0667	.0000	−.0667
130	.0614	.0088	−.0702
140	.0513	.0256	−.0769
150	.0417	.0417	−.0833

It is now proposed to remove the restriction on the weight deviations of specimens; instead of assuming the weight of the middle specimen to be equal to the average, it may now be allowed to vary over the entire range from 100 to 150 units, as shown in the Table VI.

Table VI shows the entire range of values taken by d_1, d_2, and d_3 within the specimen weight range stated above. It may be observed that the largest positive deviation, d_1, occurs when d_2 and d_3 are both negative and equal. Similarly, the largest negative deviation, d_3, occurs when d_1 and d_2 are both positive and equal. The weight deviations d_1 and d_2 can be applied to R and S values to show their effect on the quantity E. For example, the application of equation 2 to the values for water solubles in the same paper (3) gives the following results:

TABLE VII

POSITIVE VALUES OF WEIGHT VS. AREA DEVIATION, E

	Average Range ($R = 6.4^{C}_{c}$, $S = 3.0^{C}_{c}$)			Maximum Range ($R = 11.5^{C}_{c}$, $S = 5.4^{C}_{c}$)		
w_2	$\frac{d_1R}{C_c}$	$\frac{d_2S}{C_c}$	$\frac{E}{C_c}$	$\frac{d_1R}{C_c}$	$\frac{d_2S}{C_c}$	$\frac{E}{C_c}$
100	.61	−.14	.47	1.10	−.26	.84
110	.53	−.08	.45	.96	−.15	.81
120	.46	−.03	.43	.83	−.05	.78
125	.43	.00	.43	.77	.00	.77
130	.39	.03	.42	.71	.05	.76
140	.33	.08	.41	.59	.14	.73
150	.27	.13	.40	.48	.23	.71

It is apparent that the product d_1R is much larger than d_2S and that the largest value of E is obtained when d_1 is at its maximum value, i.e., when the heaviest specimen contains the highest percentage and the lightest specimen contains the lowest percentage of water solubles. It may be observed also that the variation in w_2 has only a slight effect upon E. This is explained by the relation between the deviations in which d_1 decreases as d_2 increases. Therefore, a decrease in the product d_1R is partially compensated for by an increase in d_2S.

There are two other pairs of deviations that could correspond to R and S, namely d_1 d_3 and d_2 d_3. Furthermore, either the first or second deviation in each pair might correspond to range R and the other deviation to S. It is apparent that E will be greatest when R corresponds to the largest deviation, be it either positive or negative. The calculations in Table VII were based on R corresponding to the largest positive deviation. Table VIII shows the results of computations based upon R corresponding to the

largest negative deviation d_3. Deviation d_2 was selected to correspond to S as this combination gives the largest negative values of E. The equation may be written:

$$E = d_3R + d_2S.$$

TABLE VIII

NEGATIVE VALUES OF WEIGHT VS. AREA DEVIATION, E

	Average Range			Maximum Range		
w_2	d_3R	d_2S	E	d_3R	d_2S	E
100	−.30	−.14	−.44	−.55	−.26	−.81
110	−.36	−.08	−.44	−.64	−.15	−.79
120	−.40	−.03	−.43	−.73	−.05	−.78
125	−.43	.00	−.43	−.77	.00	−.77
130	−.45	.03	−.42	−.81	.05	−.76
140	−.49	.08	−.41	−.88	.14	−.74
150	−.53	.13	−.40	−.96	.23	−.73

For the average range the largest E value is -0.44%; and for the maximum range for any tannage the largest value of E is -0.81%. It may be observed again as in Table VII that the variation in weight of the middle specimen has little effect on the value of E. The negative values of E are approximately equal (but opposite in sign) to the positive values reported above.

Further questions might be raised regarding the possibility of any other set of d, R, and S values within the limits stated above that would result in larger E values. The largest value of the product d_1R in Table VII is 1.10%. If this quantity had been combined with an S value of 0, it would have resulted in an E value of 1.10%, which is the largest possible value within the entire range. However, under these conditions the heaviest specimen must contain the highest concentration of water solubles and the two remaining specimens must be of equal weight and both must contain the minimum concentration of water solubles. Obviously, such a set of conditions is extremely unlikely, and the corresponding estimate of E is unrealistic.

In considering the maximum values of E in Tables VII and VIII, it should be recalled that all calculations are based upon deviations and ranges selected not as typical values but as extremes that would not be expected in the usual production. For this reason the computed values are much larger than those observed in Tables I to IV.

The values of E in Tables VII and VIII are considered to be conservative estimates and approximately of the same order of magnitude as the experimental errors inherent in the chemical determination of water solubles.

Therefore, it is concluded that the method of compositing specimens from the three locations, whether on a weight or area basis, has no significant effect on the results.

After a study of all available information the Committee unanimously agreed that for the sake of simplicity and to minimize sources of variation sole leather should be sampled on an equal-area basis by the use of a die.

The cooperation of the chairman and members of the ALCA Committee on Standards and Specifications is gratefully acknowledged. Special appreciation is expressed for the work and interest of J. R. Kanagy, J. H. Davis, and R. Oehler, and of A. N. Kay, R. M. Lollar, and C. G. Telander.

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Reading Habits of Chemists and Physicists to Be Studied

Under a recent National Science Foundation grant, the Operations Research Group of Case Institute of Technology will analyze the reading done by two groups of research scientists during the time they devote to scientific communication. An earlier study by the same organization demonstrated the feasibility of applying operations research techniques in this field and showed that the average industrial chemist spends more time in scientific communication than in all the rest of his scientific activities combined. The data collected in that study indicated that in 1957 he read only about one-half of one percent of the articles published in chemistry. The approximately 300 observations which caught chemists reading journal articles involved some 71 different chemical journals. Because the chemists' total time was covered by the first study, these observations of reading constituted only a small fraction of the total (about 300 out of 25,000).

The new study will be limited strictly to reading time. The sample of scientists covered, however, will be expanded to include chemists and physicists in industry, government, and universities. The purpose of the investigation is to identify and analyze both what kinds of scientific material (journal papers, books, patents, abstracts) these scientists read and the reasons behind the reading—that is, whether for general technical information, for specific technical information, or for sources of information.

A second phase of the new study, to be conducted simultaneously with the first, will involve an economic analysis of scientific journal publication. Information will be gathered on publication costs of a representative sample of scientific journals. These data, combined with information on what is read, may make possible the determination of costs per page read.

—*Science Information News*, June-July, 1959. National Science Foundation, Washington, D. C.

LIFE LINES

Brief Biographies of Our Contributors

Dr. Seymour S. Kremen received his Bachelor's degree from the College of the City of New York, his Master's degree from New York University, and his Doctor's degree from the University of Cincinnati. He was a member of the staff of the Tanners' Council Research Laboratory at the University of Cincinnati from 1946 to 1954 with the final rank of Associate Professor. During World War II he first came in contact with the leather industry while in charge of an Army inspection group at the Graton & Knight Co., and this was followed by military service in the U.S. Navy in airborne electronics. He has been a member of ALCA since 1947 and received the Winheim Award in 1953. He has been author and coauthor of several previous contributions to *JALCA*. He is presently the General Manager of the Leather Research Corporation.

Charles W. Mann—See last month's *Journal*.

F. R. Morgan has been a Senior Scientific Officer with the British Leather Manufacturers' Research Association since 1953. He was educated at Southampton University and London University. From the latter he received a Bachelor of Science degree in physics and pure and applied mathematics in 1951 and a Bachelor of Science special degree in physics in 1952. His present fundamental research on collagen and leather fibers will form the basis of a thesis in partial fulfillment of a Doctor of Philosophy degree from London University. Mr. Morgan has worked on several applied research topics such as the development of laboratory test methods and work on improving the water resistance of upper leather.

Robert Lee Southwood received his A.B. degree from the University of Kentucky in 1949. Following this he served as a high-school science teacher for two years. His association with leather technology began with his employment at the Tanners' Council Research Laboratory at the University of Cincinnati in 1951 which continued until 1954 when he left to assume his present position with the Leather Research Corporation. He has been the coauthor of several previous contributions to *JALCA*.

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Proceedings, Reports, Notices, and News

of the

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The Officers and Council of the Association join the editorial staff in extending to all members the warmest of season's greetings and sincere wishes for a happy, prosperous and peaceful New Year.

EMPLOYMENT NOTICE

CHEMIST WANTED.—A Midwestern tanner desires a chemist capable of analytical and control work in side upper leather. Man with experience desired. Write fully and address to Box L-200, c/o Secretary, American Leather Chemists Association, University of Cincinnati, Cincinnati 21, Ohio.

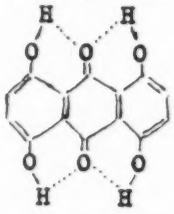
ABSTRACTS

Preparation of Upper Leather with Masked Chrome Liquors. P. J. van Vlimmeren. *Das Leder*, **10,** 121–25 (1959).—Fuller leather is produced with glucose-reduced than with SO_2-reduced chrome liquors if they are 33% basic, but there is little difference if the liquors are 42% basic. In the series of tannages, (1) normal acid pickle, normal basicity chrome liquor, (2) normal pickle, masked liquor, (3) strongly acid pickle, highly basic liquor, and (4) strongly acid pickle, masked chrome liquor, there was a shift in leather quality from (1) to (4) in favor of the SO_2-reduced liquor. Formate-masked liquors should be made by adding the formate to the hot chrome liquor during its preparation. Addition of the formate to the pickle liquor or to the cold chrome liquor at the start of tanning is not satisfactory. The reaction of formate with the chrome salt is slow at ordinary temperatures. Theis used 3 moles of formate per mole of Cr_2O_3 but did not allow time for the reaction. At boiling temperature the reaction is rapid, and 0.5 mole of formate will make better leather than 3 moles as used by Theis. A process for making "Rind box" upper leather is as follows: Soak salted sides 1 day; remove hair in 24 hours with sulfide-lime; delime for 15 minutes with 0.3% (hide weight) of hydrochloric acid added in portions, then with 1% ammonium sulfate for about 0.5 hour; pickle overnight in 100% float, 7% salt, and 1.25% sulfuric acid; tan in 45% water, 1.5% salt, and all chrome liquor added at once; drum 2 hours; neutralize during 4 hours; then drum 1–1.5 hours more; after at least 48 hours, wring and shave. Toggled leather should contain 2–2.5% Cr_2O_3, and that for pasting, 2.5–3%. Prepare the chrome liquor by adding slowly, with violent stirring, a 10% soda solution to the boiling chrome solution until it is 42% basic, then add 0.5 mole (per mole Cr_2O_3) of sodium formate in 10% solution, hold at 100°C. for 1 hour, then cool overnight. In a 35% float the pH should be 2.9–3.0. Masked liquors have the advantage over unmasked liquors of lower astringency; rapid, uniform penetration; even distribution of chrome; smooth grain; and greater area yield. Phthalate-masked (0.1 mole), highly basic liquors made good leather, although not as good as that made with formate-masked liquors. Phthalate should be added at the time neutralization is normally done. Masking with either acetate or oxalate was possible and is being investigated further.

I.D.C.

The Relation between Constitution and Tanning Action of Phenolic Tannins. A. Küntzel, H. Rosenbusch, and H. El Sissi. *Das Leder*, **10,** 133–37 (1959).—The purpose of the study was to learn if intramolecular hydrogen bonds between a proton-donating phenolic OH group and a neighboring proton

receptor in the same molecule would decrease the affinity of the compound for hide substance. Natural tannins, which are complex mixtures, are not suitable for such studies. Polyaromatic hydroxyl compounds and their reduced forms were used and their affinities for the adsorbents (collagen, silica gel, and cellulose) were investigated chromographically. Tetrahydroxyanthraquinone,



with all OH groups in the ortho position, has little affinity for hide substance because all OH groups are inactivated. After reduction, the affinity for hide is much greater because hydrogen bonding to a quinone group is then not possible. 1,5-dihydroxyanthraquinone had no affinity for hide substance, but after reduction with $SnCl_2$ to 1,5-dihydroxyanthranol it was strongly adsorbed. The following R_f values were found by chromatography on special S&S 2043b paper (1) before reduction and (2) after reduction of the compound: 1,5-dihydroxyanthraquinone, .94 and .104 resp.; 1,2,3-trihydroxyanthraquinone, .84 and .327; 1,2,4-trihydroxyanthraquinone, .94 and .101; and 1,2,5,8-tetrahydroxyanthraquinone, .642 and .22. The 2,4-dihydroxy derivatives of the compounds benzhydrol, phenylmethane, phenylsulfone, and benzophenone were adsorbed on a hide powder column with decreasing affinity. After the column was removed and divided into four parts, each zone was extracted with dimethylformamide, and the adsorbed material was identified by chromatography on S&S 2043b paper. R_f values of the four derivitaves, in the order given above, were as follows: 0.00, 0.15, 0.29, and 0.89. Tu and Lollar (*JALCA*, **45**, 324 [1950]) state that 2,4-dihydroxybenzhydrol tans and 2,4-dihydroxybenzophenone does not tan because quinoid resonance is possible only in the former. If this theory were true there should be a similar difference between the 4,4'-dihydroxy derivatives of diphenylmethane and benzophenone, but this is not the case. Natural dyes, which have some of the characteristics of the tannins, contain simpler compounds. Fustic contains maclurin and morin which have only slight affinity for hide substance. After reduction of fustic extract, however, with Raney nickel at high pressure its affinity for hide was much increased, and purity of the extract was increased from 59.1 to 94.2. Catechin is a reduction product of quercetin. R_f values for quercetin were 0.74–0.45 and for d-catechin, 0.35–0.25. I.D.C.

Finishing of Upper Leathers. J. K. De. *J. Indian Leather Technol. Assoc.*, **7**, 121–30 (1959).—Description, with many formulas. H.B.M.

Vegetable Tanning with the Use of Sulfite Cellulose Extract. G. D. Pande and R. K. Agarwal. *J. Indian Leather Technol. Assoc.*, **7**, 131–33 (1959).—Sides are pickled, pretanned in a lignosulfonate extract in the presence of salt until struck through, then tanned with vegetables extracts in a series of suspenders and layers. Composition of the resulting leather is much like that of ordinary vegetable-tanned leather. H.B.M.

Pretreatment with Calgon (Phosphate Glass 696) for Chrome Tanning of Upper Leather. S. P. Ghosh, S. N. Bose, and K. T. Sarkar. *Bull. Central Leather Research Inst., Madras*, **5**, 457–62 (1959).—Bated skins are treated with 3.5% phosphate glass 696 in 80% water, followed after 30 min. by enough H_2SO_4 to reduce the pH value to 2.6–3.0 after 8 hr. The stock is rinsed, then Cr-tanned by a conventional process. Formulas are given for dehairing, deliming and bating, Calgon treatment, tanning, coloring, fatliquoring and finishing operations. The Calgon pretannange is alleged to give fuller flanks and tighter, smoother grain. H.B.M.

Sulfonation and Sulfation. E. G. Gilbert and E. P. Jones. *Ind. Eng. Chem.*, **51**, 1143–54 (1959).—A review of progress in 1958 with many references. H.B.M.

Differences between Metacollagen and Collastromine. I. Banga and J. Balo. *Acta Physiol. Acad. Sci. Hung.*, **15**, 127–31 (In English); *Chem. Abstr.*, **53**, 15157*h*.

Amino Acid Sequences in Gelatin. F. M. Robbins. *Univ. Microfilms* (Ann Arbor, Mich.) *L. C. Card* No. **Mic 59-883**, 150 pp.; *Dissertation Abstr.*, **19**, 2454 (1959); *Chem. Abstr.*, **53**, 15169*e*.

Melting of Collagen under Stress and Its Elasticity in the Amorphous State. O. K. Spurr, Jr. *Univ. Microfilms* (Ann Arbor, Mich.) *L. C. Card* No. **Mic 59-1526**, 149 pp.; *Dissertation Abstr.*, **19**, 2783 (1959); *Chem. Abstr.*, **19**, 2783 (1959); *Chem. Abstr.*, **53**, 15169*g*.

Better Way to Lead-Line Your Wooden Tanks. A. E. Hughes. *Chem. Eng.*, **66**, No. 18, 158 (1959).—The vertical sheets are secured to the wood by lead tabs burnt to the lead sheets and passing through holes cut in the wooden tank wall. H.B.M.

Leather Research in Germany. A. Küntzel. *J. Soc. Leather Trades Chemists*, **43**, 231–37, (1959).—Leather research and technological problems in West Germany subsequent to the Second World War are reviewed, and a description of the laboratories involved is given. J.M.C.

Synthetic Resin Dispersions for Leather Finishing. J. Handscomb. *J. Soc. Leather Trades Chemists*, **43**, 237–55, (1959).—The properties of a number of synthetic resin latices and of simple pigmented finishes derived therefrom are reviewed. Discussion, based mainly on laboratory work, is restricted to the specific dispersions examined. Several new tests devised for measuring the performance of finishes are described in detail. These include a wet- and dry-rub fastness test and an adhesion test in which wetted leather finish was scraped with a scalpel. Aging of finishes by outdoor and indoor exposure, exposure to ultraviolet light, and in an oven at 50°C. is also discussed. A butadiene – methyl methacrylate copolymer dispersion provides a low-cost binder with adequate properties for many applications. J.M.C.

A Note on the Viscosity of Black Wattle–Extract Solutions: The Relation between Viscosity and pH. S. Evelyn. *J. Soc. Leather Trades Chemists*, **43**, 255–59, (1959).—A preliminary study of the viscosity of commercial wattle-extract solutions adjusted to various pH levels below 7 was made at three concentrations. The viscosity in water of the methanol-soluble portion of a commercial wattle extract was examined at one concentration. A linear relationship between viscosity and pH (pH 2.5–pH 6.5) was established at each concentration of commercial wattle extract. The increase in viscosity with increase in pH was observed to be concentration-dependent. J.M.C.

A Note on Rapid Test Methods for Predicting the Durability of Chrome-Vegetable-tanned Leathers. R. Sykes and D. Williams-Wynn. *J. Soc. Leather Trades Chemists*, **43**, 265–70, (1959).—Storage of fatliquored, retanned chrome leather for 3 weeks at 50°C. and 95% R.H. resulted in approximately the same deterioration as storage for 8–9 months at 20°C. and 65% R.H. Deterioration is estimated by buckle-tear and grain-crack measurements. Some retan leather containing a high content of organic anions did not deteriorate when exposed to the longer, less severe conditions but did show deterioration in the accelerated test. The stronger the masking action of the organic anion, the more stable is the retanned leather produced. The deterioration of chrome-retanned leather is associated with the formation of acidity through displacement of strong acid anions from the chromium complex present in leather. Deterioration is accelerated if the original leather is comparatively acid. J.M.C.

Studies in the Tanning Action of Chromium Sulfate Masked with Amino Acids. R. Sykes. *J. Soc. Leather Trades Chemists*, **43**, 270–77, (1959).—The corium of sheepskin, after liming, deliming, and elimination of salts, was reacted with complexes formed between chromium sulfate and α-, β-, γ-, and ϵ-amino acids. A pressing technique removed most of the chromium held in the bound water of the leather. Shrinkage temperature was determined on the leather after 2 months of aging. Under comparable conditions of pH and with the same molar ratio of amino acid to chromium, fixation of chromium by collagen is greatest when an α-amino acid is used for masking and least when an ϵ-amino acid is used. Coordination of the amino acid to chromium is only through the carboxyl group. The stability of the coordinate bond formed between the amino acid and the carboxyl group is proportional to the pK value of the amino acid. In chrome tannage under aqueous acid conditions there can be no appreciable coordination of the amino group of collagen to chromium. J.M.C.

Investigations on Bating. VII. The Influence of Bating Conditions on Goatskins Tanned for Glacé Kid. G. Green and R. Mitton. *J. Soc. Leather Trades Chemists*, **43**, 277–90, (1959).—Goatskins were bated for glacé kid leather in a statistically planned experiment with variations in duration, temperature, pH, concentration, and type of bate. The skins were examined for various properties in the bated, chrome crust, and finished leather states. Air permeability of the bated pelts was a function of pH rather than degree of bating. Smoothness of grain in the bated pelts and flatness of the grain of the crust leather were increased by increased concentration of

bate, time, and temperature. The over-all quality of the finished leather as assessed by the warehouse grading was hardly affected by a wide variation in bating condtions, but individual properties were significantly affected in many cases. It is concluded that the bating process of goatskins for glacé kid can be varied within very wide limits without a great deal of influence on the resultant leather. J.M.C.

Tear Tests of Leather. R. Mitton and F. Morgan. *J. Soc. Leather Trades Chemists*, **43**, 290–93. (1959).—The buckle-tear test (the official test of the S.L.T.C.) is compared with a new tear test, the Baumann Test, which may become the Official Method of the International Union of Leather Chemists Societies. Considerably higher values are given by the buckle-tear than by the Baumann Test but there is extremely close correlation between the results. In the Baumann Test two pieces of iron, 1 cm. wide and 1 mm. thick, are inserted in a 2-cm. slit (lengthwise) in the 5 x 2 cm. leather sample. The tensile strength machine separates the pieces of iron, tearing the leather. The mode of tearing in Baumann's test appears to be much the same on all the leathers for which it can be used, whereas tearing occurs in various ways in the buckle-tear test. The Baumann Test is a little more rapid and convenient than the buckle-tear test for light leathers, but it is not applicable to heavy leathers, as is the buckle-tear test. J.M.C.

Application of a Sequential-Type Analysis to Field Tests. H. R. Rush. *Textile Research J.*, **29**, 628–31 (1959).—For the determination of the durability of fabrics under field-test situations a sequential-type approach to analysis of the data obtained was devised. With this information a decision can be made as to the best time to stop testing without loss of meaningful information. Adaptation of the method to other field tests appears feasible. C.L.D.

Effect of Alkali on the Extractability of Wool Proteins; Evidence against Disulfide Exchange as an Explanation for the Reduction in Solubility. J. M. Swan. *Textile Research J.*, **29**, 665–67 (1959).—Data are presented on the solubilities of chemically altered wools which do not support the disulfide-exchange hypothesis. It is suggested that configurational changes leading to new, less soluble, hydrogen-bonded structures may occur when wool is chemically treated. C.L.D.

Some Unusual Outgrowths from Secondary Follicles in Soay Sheep. M. L. Ryder. *Nature*, **183**, 1831–32 (1959).—Some "plugs" of undifferentiated cells were discovered in preparations of skins of Soay lambs and adults. The plugs were at the sebaceous gland level, each joined on to the ectal side of a secondary follicle. Most of the outgrowths traced had a lumen extending 60 to 80μ below their attachment. This joined the follicle lumen and was either lined or blocked with stratum corneum in the upper part; below this it was blocked discontinuously with pigment. On termination of the lumen at the sebaceous gland level of the parent follicle the cells of the outgrowth become undifferentiated on the side adjacent to the follicle, but on the opposite side they had the appearance of sebaceous cells. The outgrowths resemble developing follicles but can be differentiated from them. C.L.D.

PATENTS

Tanning Process for Hides and Furs. U.S. Pat. 2,890,096. R. Heyden, Dusseldorf, J. Plapper, Dusseldorf-Holthausen, and F. Schmitt, Dusseldorf, Germany, assignors to Bohme Fettchemie G.m.b.H., Dusseldorf, Germany. Appl. August 4, 1953. Claims priority, appl. Germany, August 11, 1952.—1. A process for tanning hides and furs which comprises applying thereto as a tanning agent a water-soluble resinous condensation product obtained by condensing an organic sulfonamide selected from the group of compounds consisting of unsubstituted and alkyl substituted monosulfonamides and polysulfonamides of aromatic hydrocarbons with formaldehyde and with dicyandiamide, converting the said water-soluble resinous condensates into insoluble form and finishing the tanned materials in the usual manner.

Modified Animal Glue and Method of Preparation. U. S. Pat. 2,900,267. E. F. Cavanaugh, Wilmette, and H. L. Keil, Clarendon Hills, Ill., assignors to Armour and Company, Chicago, Ill., a corporation of Illinois. Appl. October 17, 1956.—12. As a new composition of matter, animal glue esterified in a non-alkaline aqueous reaction medium with from 10 to 30% by weight of an alkylene oxide selected from the group consisting of styrene oxide, ethylene oxide and propylene oxide, said esterified animal glue as compared with its properties prior to esterification being characterized by a reduced gelling temperature, by increased solubility in water, and by appreciable solubility in polar organic solvents, said esterified animal glue being adjusted to an acidity within the pH range of 4 to 6.

Method of Dehydrating with Organic Solvent and then Vegetable Tanning of Untanned Skins. U. S. Pat. 2,906,591. A. E. Ushakoff, Beverly, Mass., assignor, by mesne assignments, to N. W. Levin, New York, N. Y., A. E. Ushakoff, care of Seco Venture, Somerville, Mass., and J. B. Hatton, care of Eagle-Ottawa Leather Co., Grand Haven, Mich., as trustees. Appl. June 21, 1954.—1. A method of tanning skins under substantially nonaqueous conditions consisting essentially of contacting an untanned water-wet skin with an inert water-miscible organic solvent until substantially all the water from the skin is extracted and replaced by said solvent, then processing the skin in the absence of water with the steps of impregnating the skin with an inert organic solvent solution of a vegetable tanning at an acidity of the skin such that the tannin is introduced into the skin, controlling the acidity of the skin until the tannin impregnated skin is brought to an acidity corresponding to a pH of more than 6, the tannin is distributed through the skin and the skin remains essentially untanned, then finally adding an acidic reagent to the skin to bring the final acidity of the skin to correspond to a pH of between 2.0 and 6.0 and drying the skin to remove organic solvent so that the skin is tanned.

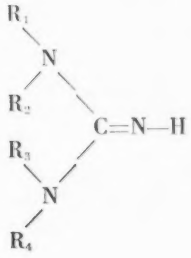
Dyeing Animal Fibres and Compositions Therefor. U. S. Pat. 2,904,385. R. Charle, Soisy-sous-Montmorency, and R. Lazare Lantz, Paris, France, assignors to Société Anonyme dite Societe Monsavon-L'-Oreal, Paris, France, a corporation of France. Appl. July 15, 1957. Claims priority, appl. France, July 17, 1956.—2. Process for dyeing animal fibres which comprises treating the animal fibres with an aqueous solution at pH 7 to 11 containing

at least one azo dye having in its molecule at least one disulphide group, and a reducing agent selected from the group consisting of lower aliphatic mercapto carboxylic acids, alkali metal hydrosulphites, sulphites, boro-hydrides and thiourea dioxide.

Preparation of Long-Chain Alkylhalosilanes. U. S. Pat. 2,888,476. E. L. Little, Wilmington, and G. M. Whitman, Hockessin, Del., assignors to E. I. du Pont de Nemours and Company, Wilmington, Del., a corporation of Delaware. Appl. August 1, 1956.—1. The process of synthesizing organohalosilanes at least some of which have carbon chains longer than those of the compounds from which they are made which consists of reacting a member of the group consisting of alkyl and cycloalkyl chlorides, bromides and iodides having 1–8 carbon atoms with a silicide of the group consisting of the alkali and alkaline earth metal silicides at a temperature of about 200°–500°C. Used for water-proofing leather.

Process of Retanning Leather with Condensation Products of Phenols, Amines, and Formaldehyde. U. S. Pat. 2,890,095. M. Meister, Leverkusen, G. Mauthe, Opladen, and K. Faber, Koln-Stammheim, Germany, assignors to Farbenfabriken Bayer Aktiengesellschaft, Leverkusen, Germany, a corporation of Germany. Appl. March 16, 1954. Claims priority, appl. Germany, March 25, 1953.—1. A retanning process which comprises retanning pretanned leather with an aqueous solution of an acid-soluble, cationic retanning agent obtained essentially from a condensation in an alkaline medium at a temperature up to about 100°C. of (1) a member of the group consisting of phenol, chlorophenol, cresol, 4,4′-dihydroxydiphenyl-dimethylmethane, and cyclohexyl phenol (2) an amine having the formula HNR_1R_2 wherein R_1 is a member of the group consisting of hydrogen, lower alkyl, and hydroxy-lower alkyl, and R_2 is a member of the group consisting of lower alkyl and morpholino, and (3) formaldehyde, 1–2 mols of the amine and from 1.5–2 mols of formaldehyde being employed per one mol of the phenolic compound, said retanning starting at a pH within the range of about 3.5 to 4.5 and finishing at a pH within the range of about 5 to 7.

Dyeing Proteinaceous and Nylon Materials. U. S. Pat. 2,900,218. C. J. Gray, Clemson, S. C., assignor to Deering Milliken Research Corporation, Pendleton, S. C., a corporation of Delaware. Appl. February 7, 1956.—1. In a process for dyeing with high affinity milling colors textile fibers selected from the group consisting of nylon and proteinaceous fibers, the improvement which comprises adding to the bath in which the fibers are dyed a guanidine compound selected from the group consisting of bases represented by the formula:



wherein R_1, R_2 and R_3 represent members selected from the group consisting of hydrogen, monocyclic aromatic radicals, aliphatic radicals, and cycloalkyl radicals, and R_4 represents a radical selected from the group consisting of monocyclic aromatic, aliphatic and cycloalkyl radicals; and acid addition salts thereof.

Organosilicon Compositions Containing Beta-Dicarbonyl Zirconium Compounds and Leather Article Treated Therewith. U. S. Pat. 2,884,393. J. W. Gilkey, Midland, Mich., assignor to Dow Corning Corporation, Midland, Mich., a corporation of Michigan. Appl. January 23, 1957.—1. A composition of matter comprising (1) from 15 to 50% by weight of a compound of the formula

$$\left[\begin{array}{l} RC{-}O{-} \\ \quad\| \\ R'C \\ \quad| \\ R''C{=}O \end{array}\right] ZrY_{4-n}$$

in which R is an aliphatic hydrocarbon radical, R' is selected from the group consisting of aliphatic hydrocarbon radicals and hydrogen atoms, R'' is selected from the group consisting of aliphatic hydrocarbon radicals and aliphatic hydrocarbonoxy radicals, n has a value from .75 to 4 inclusive and Y is selected from the group consisting of aliphatic hydrocarbonoxy radicals and oxygen atoms, (2) from 5 to 70% by weight of a methylpolysiloxane resin composed of trimethylsiloxy units and SiO_2 units in such proportion that the ratio of methyl radicals to silicon atoms is from 1:1 to 1.5:1 and (3) from 5 to 80% by weight of a polysiloxane having the general formula

$$Z_mSiO_{\frac{4-m}{2}}$$

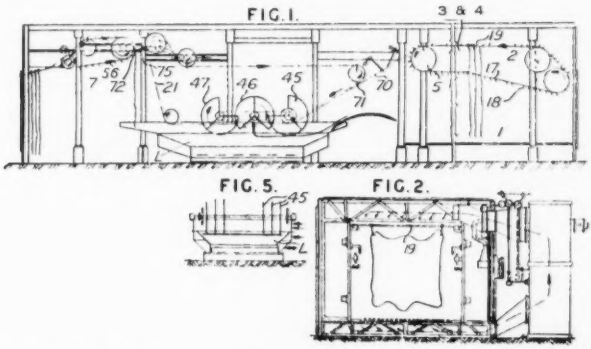
in which Z is a hydrocarbon radical of less than 7 carbon atoms and m has an average value from 2 to 2.9 inclusive. Used to improve water repellency.

Phosphorus Containing Aziridinyl-Alcohol Polymers and Flame Resistant Organic Textiles. U. S. Pat. 2,886,538. L. H. Chance, G. L. Drake, Jr., and W. A. Reeves, New Orleans, La., assignors to the United States of America as represented by the Secretary of Agriculture. Appl. June 5, 1956.—1. A process for producing flame resistant polymers which comprises heating a mixture of an aziridinyl compound selected from the group consisting of 1-aziridinyl phosphine oxides and sulfides and an alcohol having the formula, $R(OH)_x$, where x is an integer of at least 2 and R is an alkyl radical, the proportions of alcohol and aziridinyl compound in said mixture being such that from 1 to 2 alcoholic —OH groups are present for each 1-aziridinyl group, and continuing heating until said aziridinyl compound and said alcohol have reacted with each other to produce a polymeric reaction product. Useful as leather-treating agents.

Process for the Dressing of Leather. U. S. Pat. 2,887,410. W. Graulich, Leverkusen-Bayerwerk, G. Mauthe, Opladen, and K. Eitel, Leverkusen, Germany, assignors to Farbenfabriken Bayer Aktiengesellschaft, Leverkusen,

Germany, a corporation of Germany. Appl. January 21, 1955. Claims priority, appl. Germany, January 21, 1954.—1. A process of dressing leather wherein the leather is first coated with a composition containing a single copolymer, said copolymer derived essentially from butadiene and acrylonitrile, said copolymer having an oily-viscous consistency and a Defo hardness no greater than 0.

Impregnating Leather with Fat. Brit. Pat. 813,691. Svit, Narodni Podnik. Appl. Nov. 25, 1955.—A plant for impregnating tanned skins comprises a tunnel-like enclosed housing through which the skins pass suspended from rods supported by a separate chain conveyer for each of three zones, viz. a drying and heating zone, an impregnating zone in which the skins are immersed in liquid fat and a setting zone, and transfer devices for the rods from one conveyer to the next. As shown in Fig. 1, a skin is admitted through the right-hand end of the tunnel and placed on a pair of conveying chains 17 in the manner shown in Fig. 2. It is passed successively through a pre-drying zone 2, drying zones 3 and 4 and a pre-heating zone 5 on said chains and is then transferred to a second chain 21 by means of a pair of rails 70 and associated apparatus, and passes through the tank L containing fat. The rod rests upon rails below the edges of said tank and rotating discs 45, 46 and 47 serve to immerse the leather in the fat. Each disc has a cut-away portion and is



rotated so that said cut-away portion corresponds with the position of the rod, the passage of which is not therefore hindered. The rod is lifted by means of chains 21 and associated rails (not shown) from tank L and transferred to a further pair of chains 56 which carry it into the setting zone where the fat penetrates through the skin and excess fat drips off.

Paper Containing Synthetic Resins; Proofing Paper Against Water, Grease, &c.; Laminates. Brit. Pat. 813,548. Rohm and Haas Co. Appl. July 26, 1956.—Paper, e.g. thin porous tissue, made from sulphite or kraft pulp, α-cellulose fibres or rags, &c., e.g. including potentially adhesive fibres such as vinyl or acrylic polymers or cellulosic fibres coated with melamine- or urea-formaldehyde, or regenerated cellulose &c. and which may be given high wet strength by incorporating 1 to 3 per cent of melamine- or urea form-

aldehyde condensates or polymers of ureidoethyl vinyl ethers, is impregnated as by immersion in an aqueous dispersion of a synthetic resinous addition polymer having a transition temperature of at least 45°C. so that the resinous polymer is deposited as particles in and on the paper which is then dried at a temperature which is too low for such particles to coalesce. The paper may then be subjected to heat and pressure so that it becomes partially transparent and may be protective against oil, grease, oxygen or water. It may be applied over plies of other materials, e.g. paper or paper-board, wood, unglazed ceramics, hemi-cellulose gypsum boards, felt, or leather, labels, or photographs, so that on heating and pressing, a decorative or transparent coating is formed. Alternatively, plies of wood or cardboard may be hot-pressed with an interposed ply of the paper, and are thus adhered together. The resin particle size may be 1 micron, and the weight of resin may equal 60 to 180 per cent of that of the fibres. The resin may be formed from methyl-, ethyl-, propyl-, butyl-, amyl-, hexyl-, octyl- or decyl-, acrylate, &c., or from amyl-, hexyl-octyl-, decyl-, or butoxyethyl methacrylate or other alkoxyethyl methacrylate or acrylate. Preferably the alkyl acrylates have 6 to 18 carbon atoms in the alkyl group or acrylates of primary or secondary alcohols of 1 to 5 carbon atoms may be used.

Finishing Leather; Paper Containing Cellulose Derivatives. Brit. Pat. 813,900. Mo Och Domsjo A.B. Appl. Nov. 11, 1957.—Sulphomethyl cellulose (*see* Group IV (a)), is used as a finishing agent for leather, and in the paper industry as an aid in surface treatment, impregnation and sizing of paper, as a thickener in the manufacture of lacquered and enamelled paper, and as an additive in the manufacture of greaseproof paper and cardboard.

Waterproofing. Brit. Pat. 812,505. Monsanto Chemicals Ltd. Appl. March 19, 1957.—A process for imparting water-repellency to porous or fibrous materials comprises immersing the materials in an aqueous emulsion of a silicone resin incorporating an ester of titanic acid with a dihydric alcohol as catalyst, and drying the material with heating at a temperature not exceeding 160°C. to effect the final curing and polymerization of the silicones present. Suitable silicone resins are methyl, methylphenyl, amyl and methylamyl silicones (*see* Group IV (a)). Suitable esters of titanic acid are those of ethylene glycol, diethylene glycol, polyethylene glycols, propylene glycol, 1:3 and 2:3-butanediols. A preferred titanate ester is one which has been treated with an amine or aminoalcohol to reduce its acidity (*see* Group IV (b)). The emulsion may also contain silicone oils, emulsifying agents such as the double titanate of triethanolamine and stearic acid, a tall oil-ethylene oxide condensation polymer, a polyethylene glycol alkylphenyl ether, triethanolamine oleate, and octadecylamine stearate, stabilizers such as carboxymethyl cellulose, liquid paraffin, fatty acids or alcohols, urea-formaldehyde resins, melamine resins, insecticides or fungicides. The process is suitable for the treatment of textiles, leather, paper, cardboard, masonry, wood and concrete. In examples a cotton fabric, which has first been scoured, rinsed and dried, is immersed in the silicone emulsion, which is squeezed through the fabric for 20 minutes. After wringing, the sample is dried, first at room temperature, then at 110°C. for 30 minutes and finally at 160°C., and the sample is then ironed with a hot iron. The aqueous emulsions used comprise the following: (5) an amyl silicone resin, stearylamine acetate, a titanate ester of 1:3-butanediol treated

with triethanolamine, and water; (6) a methylphenyl silicone in toluene, a tall oil ethylene oxide condensate, trichlorethylene, carboxymethylcellulose, a titanate ester of propylene glycol treated with triethanolamine, and water; (7) an emulsion as described in (5) except that the catalyst is a titanate ester of diethylene glycol treated with triethanolamine; (8) a silicone emulsion as described in (6) except that the catalyst is a titanate ester of ethylene glycol treated with triethanolamine. Specification 723,989 is referred to.

Improving Catechol-tanned Sole Leather. Brit. Pat. 813,201. N. Rauchwerger. Appl. Sept. 18, 1957.—Sole leather, in the tanning of which predominantly tanning materials of the catechol group have been employed, is improved, so far as its resistance to water absorption is concerned, by the action of fumes of an aqueous solution of ammonia or gaseous ammonia followed, when penetration of the leather is complete, by the action of fumes of formaldehyde derived from aqueous solutions of formaldehyde or paraformaldehyde, so that at least part of the soluble tanning material is transformed into insoluble material.

BOOK REVIEW

Einfuehrung in die Chemische Technologie der Lederherstellung. H. Loewe. Darmstadt: Eduard Roether Verlag, 1959. 243 pp.; cloth. 24 DM (about $5.70).—In the preface the author states that much of the book grew out of the educational articles on various aspects of leather technology inserted into every issue of *Das Leder* between 1950 and 1953. These loose-leaf "Unterrichtsblaetter" as well as the new book reflect Mr. Loewe's singular interest in teaching another generation the elements of leather chemistry.

Hermann Loewe obtained his Ph.D. under Gerngross and worked from 1921 to 1924 under Bergmann in the newly founded Kaiser Wilhelm Institute for Leather Research. He has been a prominent member on the research team of I.G. Farben, now BASF, in Ludwigshafen, for more than 30 years. Possibly because of this fame more balance in presenting technological achievements would have been desirable. Faithfully quoted is the broad spectrum of BASF trademarks including those of recent origin, but in the few areas lacking BASF research contributions time seems to have stood still or to have advanced at a snail's pace. In the section on chemical dehairing, sodium hydrosulfide is mentioned cursorily; and sodium cyanide, dimethylamine, sodium hydrosulfite, and others, not at all. Practical experience in the use of sodium or calcium formate for masking of chrome liquors is ignored in favor of BASF brands on the basis of phthalate and sulfophthalic acid. Trade names have their place in a technical book, for instance, for describing bates or syntans; but when they are nearly ubiquitous they may prejudice the young tanners against trying straight chemicals, although they may often do as well as, or better than, compounded ones offered under trade names. However, this fervor in speaking *pro domo* may be pardonable if it is equalled by a clear and eloquent presentation of the subject matter. In this respect the author has excelled. Addressing himself to an eager mind of normal intelligence without training in natural sciences, he uses basic concepts of chemistry in

discussing the various phases of making leather. He subtly introduces the reader to the dipole character of water and to the role of pi-electrons in the aromatic ring. He proceeds to explain the different nature of various tannages as skillfully as the mechanism of the fatliquoring and dyeing operations.

In the second part of the book more than in the first, space has been found to discuss recent developments, for instance, the various polymers and copolymers available today for leather finishes, including the di-isocynates. Here and there, however, obsolete ideas survive, for instance, the belief that chain polymers of formaldehyde can tan hide and also, by resinifying, cause a tender grain in the finished leather (p. 109). Since all statements, as in an introduction to general chemistry, are shrouded in anonymity, it is impossible to trace the source of those obviously based on misinformation.

The book logically begins with a chapter of 14 pages on the subject of water; 19 pages on electrolytes, 8 on oxidation and reduction, and 9 on surface-active agents follow. The next 25 pages cover histology and chemistry of the hide. The manufacture of leather is treated under five headings: beamhouse (17 pp.), tannage (63 pp.), dyeing (24 pp.), lubrication and impregnation (12 pp.), and finishing (17 pp.). A number of tables (most of them pertaining to the theoretical background used by the author), a subject index, and a list of seven books recommended for further reading fill the final pages. Since theory and practice are presented without personal references—except that Stiasny's name turns up once in connection with his pioneer invention of Neradol D (p. 142)—the usual author's index becomes superfluous.

As should be evident from this brief survey of contents, anyone with a reading knowledge of German who wants to learn more about the principles involved in tanning operations may find the answers in Loewe's "Introduction", in an unadorned and easily digestible presentation. A similar book in the English language would be highly desirable. L. Seligsberger

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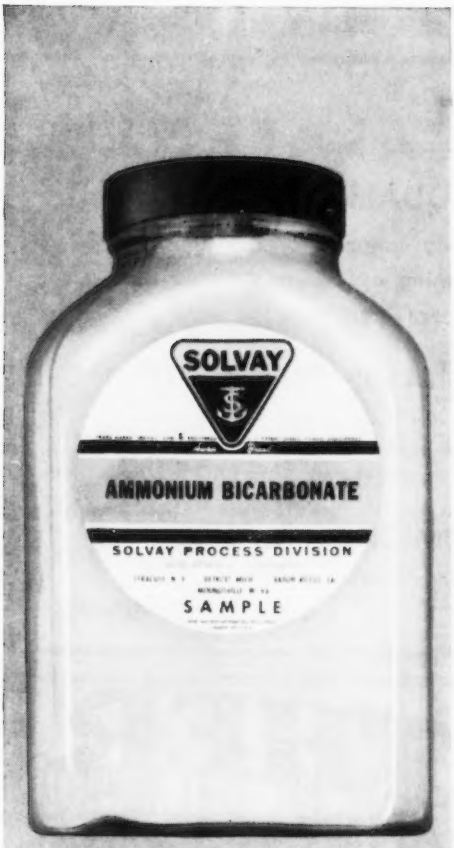

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To train Chemists in the technique of research and prepare them for Industry.

This Laboratory serves as the Official Technical Headquarters for the Tanning Industry of the United States.

Your inquiries will be gladly answered.

Address DR. FRED O'FLAHERTY, Director
Tanners' Council Laboratory
University of Cincinnati
Cincinnati 21, Ohio.

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How Tight Can You Get?

We visited a side leather tanner the other day who was wrestling with an old problem. He was trying to make a very soft straight chrome tanned side—pasted—in black and colors. As he went up percentage-wise in fatliquor using conventional sulfated oils, he finally got the softness he wanted, but by that time he had gone rag loose in the flank and belly areas of the side. The old dilemma!!

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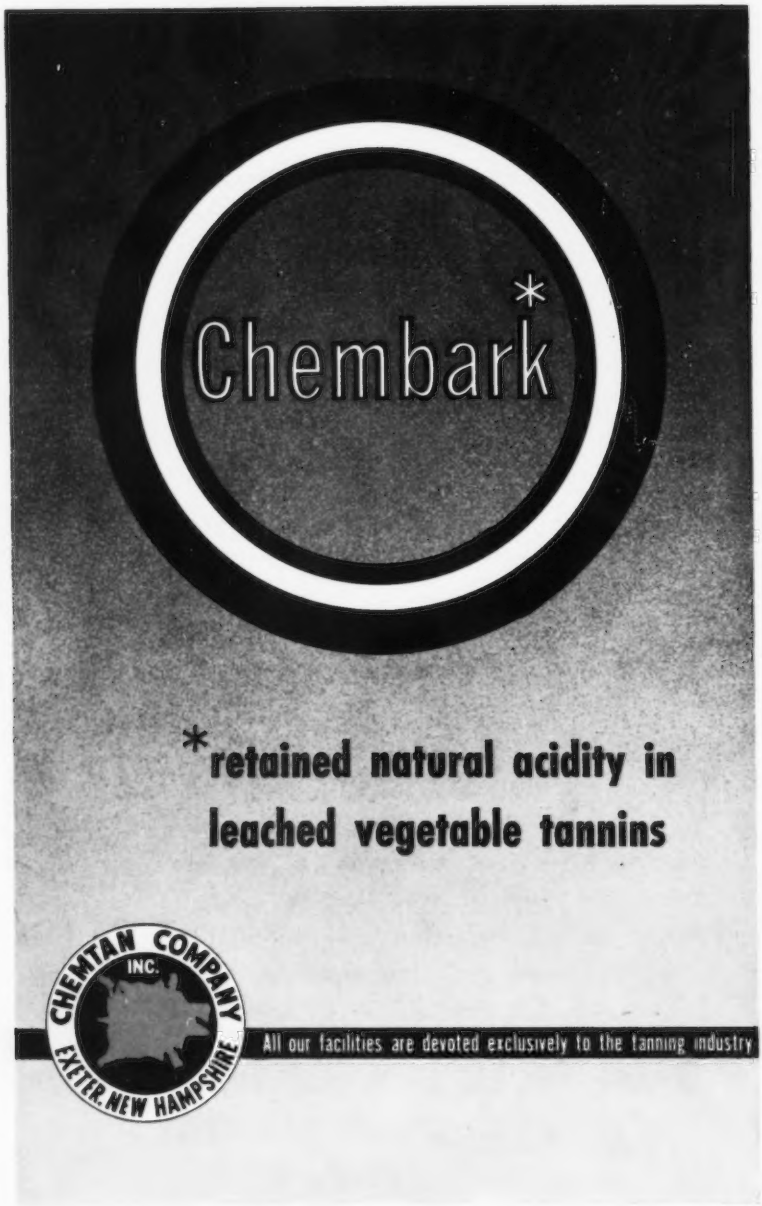
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